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Consumption and uses of crude barite and its derivatives

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C O N S U M P T I O N A N D U S E S

of

C R U D E B A R I T E

A N D I T S D E R I V A T I V E S

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(1) CONSUMPTION, PRODUCTION and PRICES of CRUDE BARITE.

Barite is a widely distributed mineral composed of barium sulphate - BaSO_4 . Its most striking feature is its weight - its specific gravity of 4.5 being about twice that of salt and many other of the colorless, transparent and vitreous minerals of its general appearance. The Mineral is usually found in a state of considerable chemical purity. However, small amounts of strontium and calcium sulphates may isomorphously replace the barium salt.

Crystals of barytes are orthorhombic; usually very perfectly developed and have a wide variety of forms. The simplest crystals are rhomb-shaped tables bounded by two faces of a basal pinacoid. The mineral has a very smooth and bright cleavage parallel to both sets of planes. The crystals may be transparent and colorless; or white and opaque; or yellow, brown, bluish or greenish in color. The mineral also occurs in a granular, earthy or stalactitic condition. Barite is of common occurrence in metalliferous veins, especially those containing ores of lead and silver.

Germany is the leading world producer of barite, followed by the United States. All other producing countries lag far behind these two leaders. About one-half of the total world output comes out of Germany. The principal German deposits are at Bad Lautenberg on the Southern rim of the Harz Mountains massif. One half of the German barite production comes from this region. Another leading center of production is Nordhausen in the Harz Mountains.

The German consumption of barite has expanded markedly in recent years as a result of heavily increased demand for barite and its derivatives in the manufacture of pigments, paints, ceramics, waterproofing and softening agents, explosives, paper, rubber goods, and other commodities. Domestic consumption of barite in pigments has increased in recent years because of official requirements for mixing the cheaper and abundantly available barium sulphate with red lead, of which there has been a shortage in Germany, and thus extending the supplies of red lead.

In international barite trade, Germany holds an even more important position than in barite production, as over half of the large German production is exported. Germany likewise has an extensive foreign trade in barium chemicals, especially lithopone, blanc fixe, artificial barium carbonate, barium chloride, and barium nitrate. Germany's export trade in barite and barium materials recorded favorable development from 1935 to 1937, but a considerable recession occurred in 1938.

The State of Missouri bears an almost identical relation to the rest of the United States in crude barite production, as Germany does to the rest of the World in the international sphere; that is, it produces about half the United States total. Missouri barite occurs at shallow depths in beds of residual clay and, excepting for periods of great activity, is usually dug by hand. In addition to clay, common impurities are iron oxide stains and masses of galena. After this material has been exposed to the sun and rain for some time, however, much of the clay becomes detached and falls off. Then hand cobbing, picking and sorting will produce a product suitable for the mills.

WORLD PRODUCTION OF CRUDE BARITE, 1926-1938 (a)

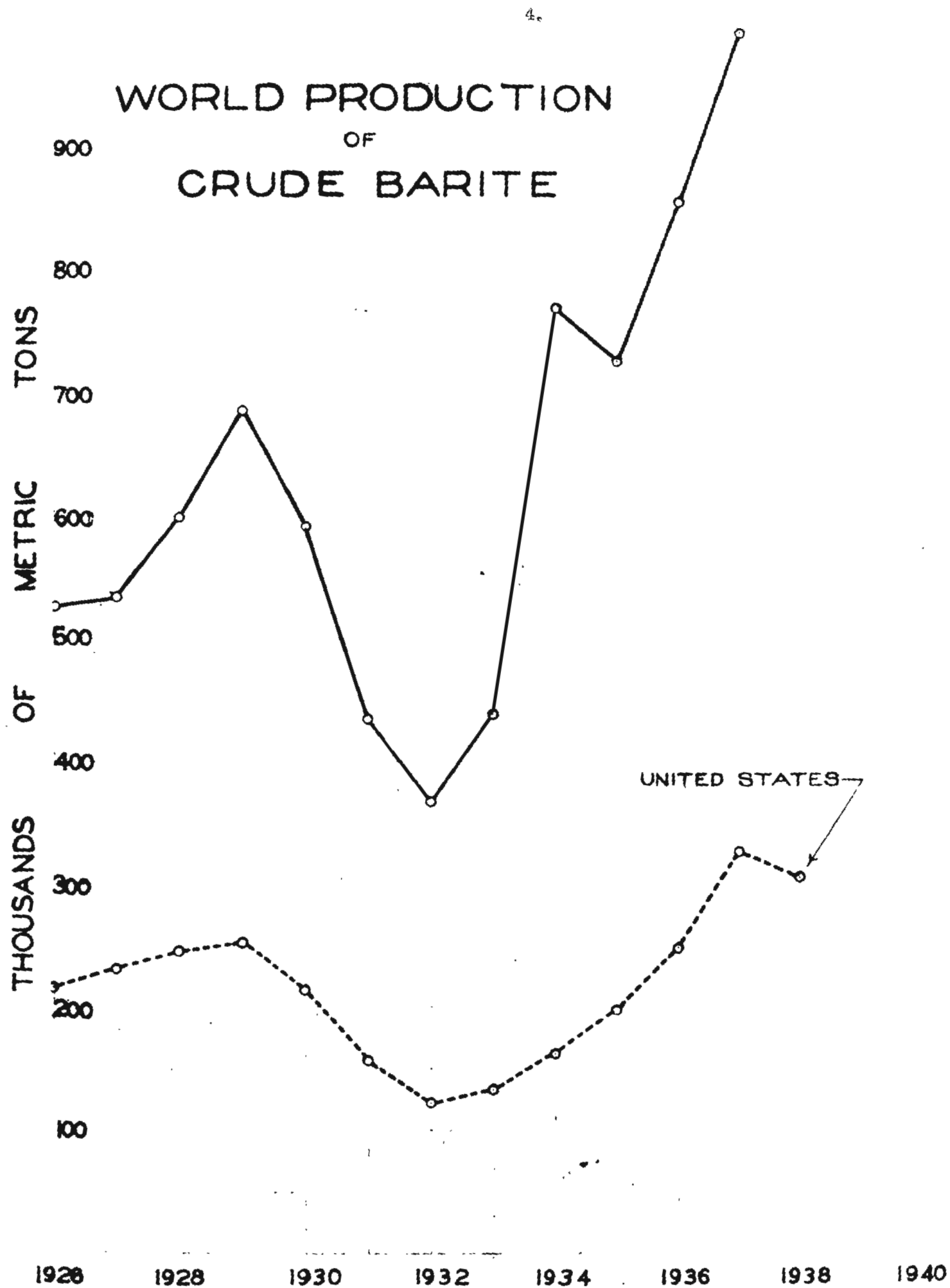
(Metric Tons)

	1926	1927	1928	1929	1930	1931	1932	1933	1934	1935	1936	1937	1938
World Production ⁽¹⁾	526,881	534,272	598,862	685,894	590,048	484,556	367,963	489,212	769,552	726,311	855,040	993,564	⁽²⁾ 960,768
Germany	162,274	174,829	256,730	286,087	236,183	170,851	110,466	147,741	354,868	347,244	⁽³⁾ 424,658	⁽³⁾ 452,388	⁽³⁾ 480,877
United States	215,795	230,664	244,525	251,533	213,126	158,321	121,174	132,813	161,806	197,525	243,624	327,380	304,298
United Kingdom	43,462	47,605	50,702	58,011	59,647	46,312	57,548	67,689	75,182	79,836	74,242	74,485	77,525
U. S. S. R.	14,389	8,501	3,480	18,930	22,500	33,000	24,300	31,000	74,800	..(4)
Italy	31,345	30,677	27,116	25,955	23,420	24,326	21,861	23,444	32,408	41,152	36,671	45,202	48,169
France	38,370	26,316	30,050	41,625	32,650	11,300	10,400	13,700	18,350	16,900	22,200	19,350	⁽⁴⁾

(a) Data published by U.S. Bureau of Mines from various official sources.

(1) Based on data from all countries reporting production. (2) Some important sources unreported.

(3) Includes production of Austria. (4) No figures released.



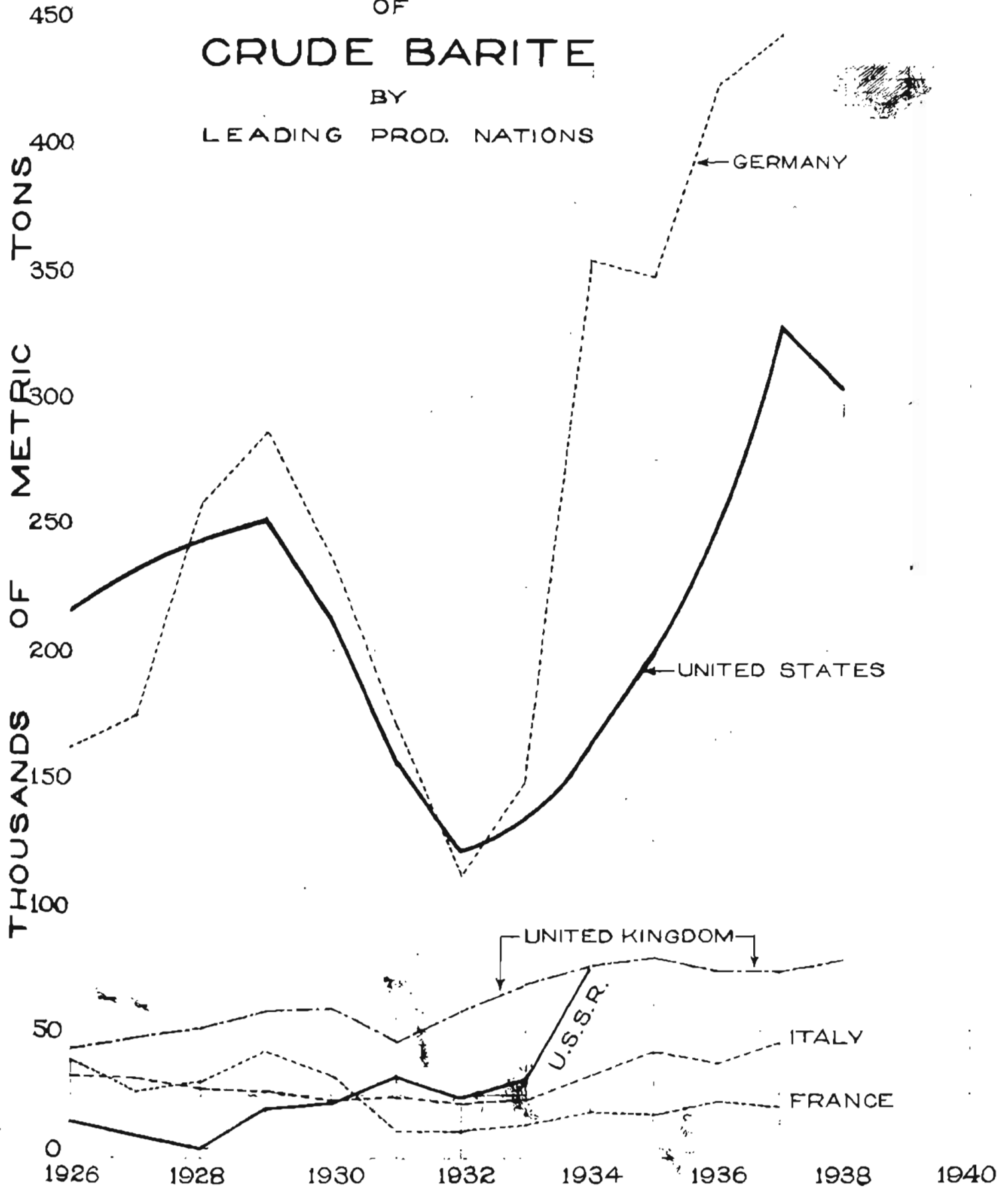
WORLD PRODUCTION

OF

CRUDE BARITE

BY

LEADING PROD. NATIONS



MISSOURI Share of United States Production of Crude Barite (a)

(On short tons).

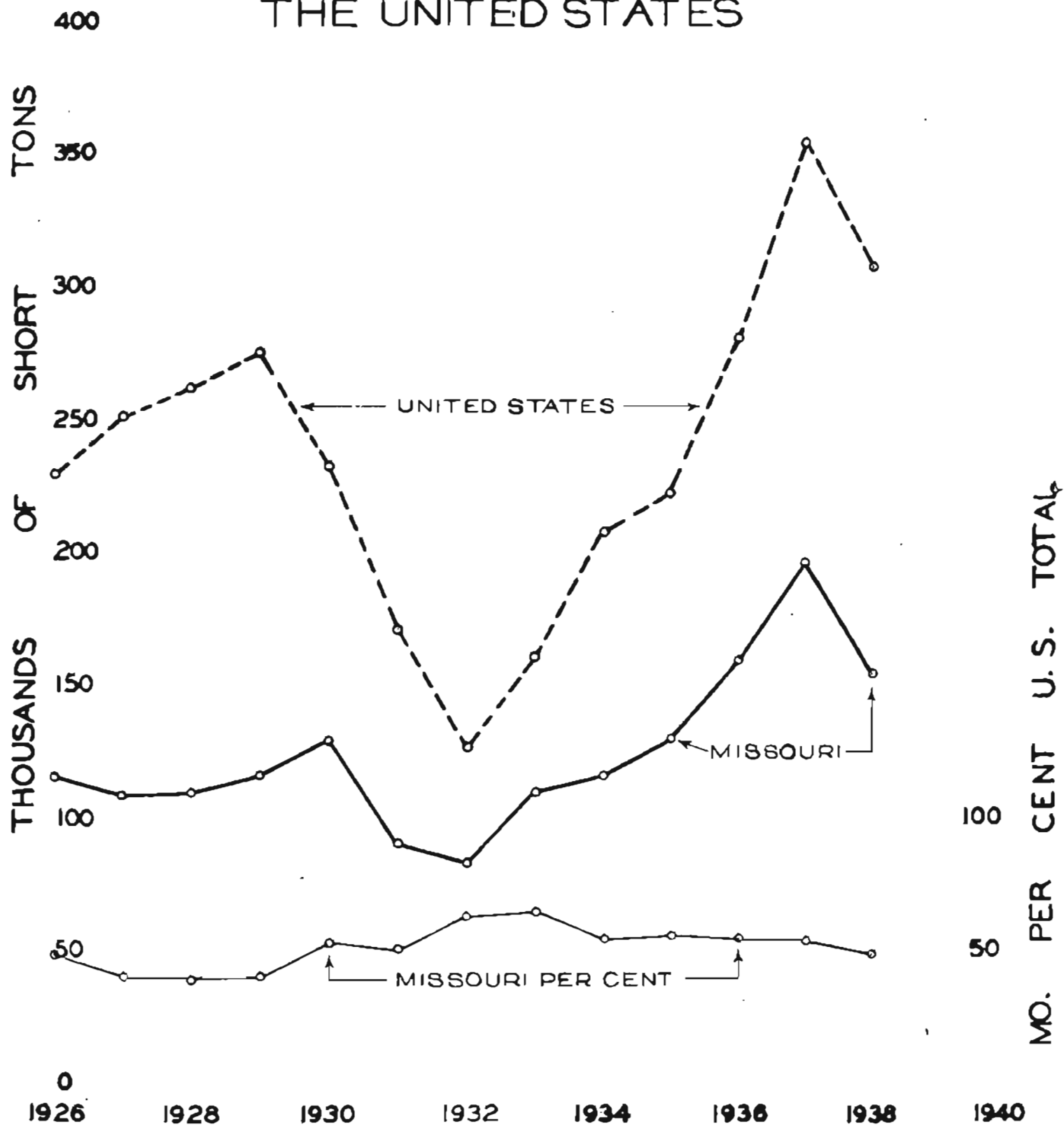
Year	United States	Missouri	Missouri Per Cent of Total.
1926	232,875.	118,919.	51.0%
1927	254,265	111,456.	43.85%
1928	269,544.	114,274.	42.5%
1929	277,269.	118,679.	42.8%
1930	234,932.	132,640.	56.5%
1931	174,520.	93,417.	53.5%
1932	129,854.	85,458.	65.8%
1933	167,8 60 .	112,335.	67.0%
1934	209,850.	118,836.	56.5%
1935	225,111.	131,921.	58.5%
1936	283,160.	160,866.	56.8%
1937	355,886.	198,101.#	55.7%
1938	309,663.	156,539.	50.6%
1939	383,609.#	171,642.	44.8%

(a) U.S. Bureau of Mines data taken from: (1) Minerals Yearbook, copies of 1932 to 1940. Articles entitled "Barite and Barium Products"; (2) The Mineral Industry (McGraw-Hill) Vols 36-38 and 40-46.

#

An all-time high in production.

MISSOURI'S SHARE OF BARITE PRODUCTION OF THE UNITED STATES



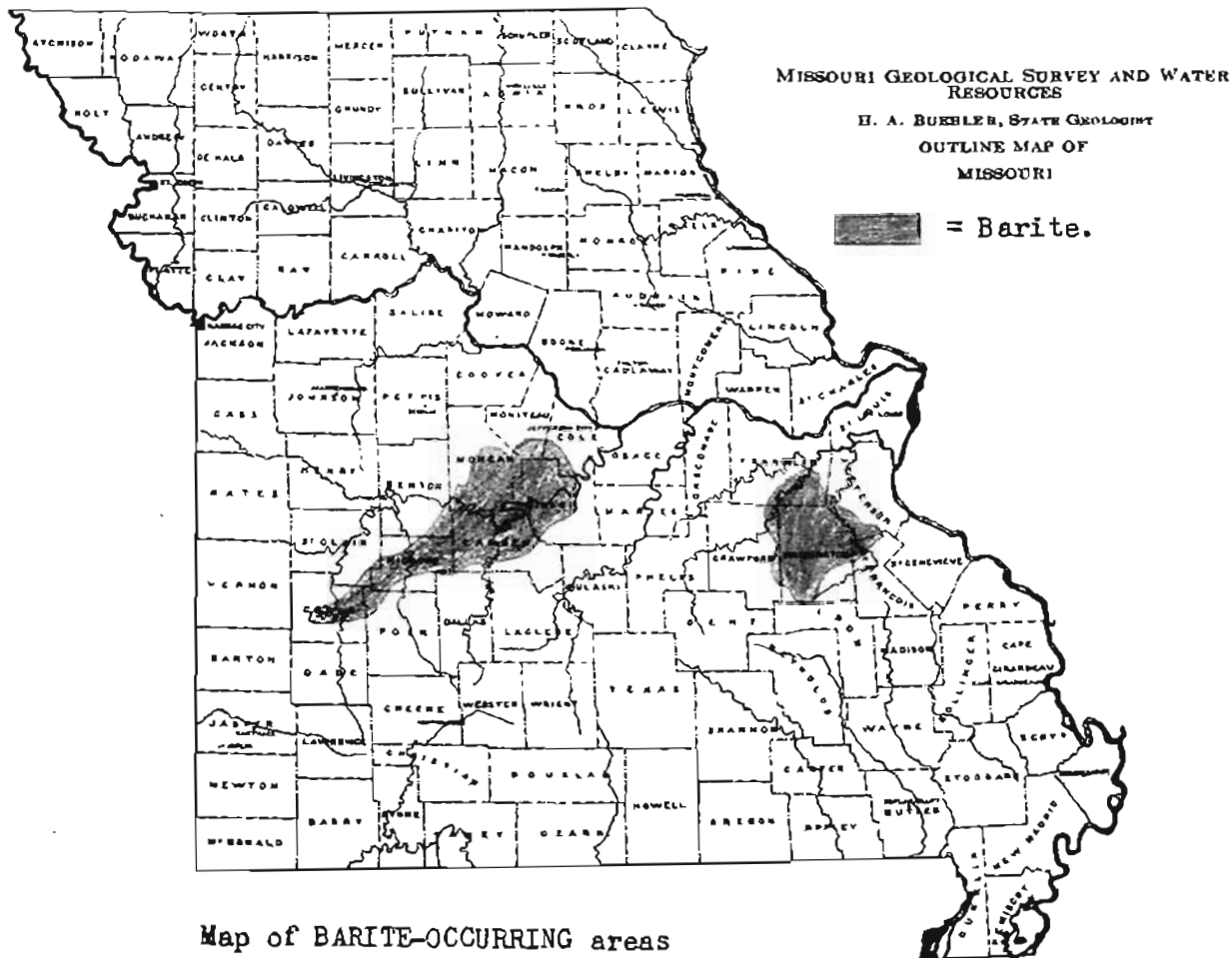
For over a decade now, Missouri has accounted for about fifty per cent of the total barite production of the United States. In 1929 this share stood at 42.5 per cent, while in 1933 it hit its maximum of 67 per cent. This latter figure does not indicate a bumper production, but only that Missouri recovered from the universal low of 1932 more rapidly than the rest of the country. In actual production, Missouri arrived at its all-time high in 1937, when it produced 198,101 short tons of barite, which was 55.7 per cent of the Nation's total.

Generally speaking, the market price of Missouri barite has been higher than the United States average as a whole - usually by a matter of half a dollar or less. In 1922, however, this price dipped well below the U.S. average. From 1930-1935 it was about the same as the U.S. average, dipping below it in 1932. In 1938 it was again higher to the extent of nearly a dollar. The market price of Missouri barite has always been well above that of the imported material.

Barite ranked eleventh in importance in mineral products of the State of Missouri in 1937. About 85 per cent of Missouri production came from Washington County that year.

THE BARITE PRODUCING AREA OF MISSOURI

The above area is shown colored in the accompanying map. It has expanded its boundaries considerably from time to time. It was mentioned in the Biennial report of the State Geologist in 1937 as follows: "For the first time in many years a relatively important district has been developed. In the vicinity of Lupus, Moniteau County, several mines have been opened and one mill erected. A



Map of BARITE-OCCURRING areas
in the State of Missouri.

steady production has been maintained and the mines are sufficiently developed to indicate deposits of considerable size. The face of one of the deposits shows barite for a depth of 50 feet, over a length of 100 feet. The McDonald Mining Company, High Grade Barium Company, and Honey Creek Mining Company are actively in operation."

The bulk of production, however, still comes from Washington County and adjacent portions of Franklin, Jefferson, and Crawford Counties. Two outlying areas are worthy of mention. One is near Wesco in Crawford County, producing from the Davis formation, and another in St. Francis County, east of Bonneterre, where the ore occurs in the Bonneterre dolomite. The Lupas district was active during 1937, but because of the slump in market conditions, production was suspended during 1938.

The accompanying table shows the annual production and values of crude barite produced during the past few years for the various producing counties in the State of Missouri. It shows the large percentage coming from the one county of Washington.

Less than one fifth of the productive area of Washington County lies within the Potosi Quadrangle, chiefly in the northeast corner. Excepting for a few scattered areas of relatively little importance, the deposits now being worked lie north of an east and west line down two miles south of Potosi; and east of a north and south line drawn four miles west of that place. The most important exception is the Palmer district, lying chiefly within a radius of five miles of the old mining town of Palmer. Another occurs on Pat, Dry, and Furnace creeks, in Secs. 11, 14, and 15 T 36 N., R 2E.

Production of Crude Barite in Missouri, by Counties, 1931-1934

County	1931		1932		1933		1934	
	Tons sold	Value	Tons sold	Value	Tons sold	Value	Tons sold	Value
Cole	4,806	\$25,090	5,297	\$26,775	575	\$ 2,446	4,555	\$ 20,496
Jefferson	16,232	99,505	8,727	40,049	2,616	11,440	9,844	56,241
St. Francois	443	2,260	407	1,413	57	2,407	138	752
Washington	68,407	392,165	70,131	391,579	107,805	491,313	92,201	452,861
*Other counties	2,877	17,389	220	811	656	1,544	3,833	15,133
Undistributed	647	2,743	676	2,720	104	401	8,215	36,406

*Other counties include Franklin, Hickory, Morgan, Miller, Camden, and Nontieau, 1931 ; Franklin and Morgan, 1932; Franklin, Hickory, Iron and Montieau, 1933; and Miller and Morgan, 1934.

Potosi, is the largest town in the district and the center of the barite industry. Other shipping points of importance are Mineral Point, Cadet, Tiff and Blackwell. Most of the good productive land has yielded from 2000 to 6000 tons to the acre; and some land has well exceeded that figure.

MINERALOGY OF THE DEPOSIT AND MODE OF OCCURRENCE
OF BARITE IN MISSOURI.

Minerals of the Missouri barite deposits are:-

- (a) Barite, itself, - BaSO_4 - known variously as barite, barytes, heavy spar, and, locally, as tiff.
- (b) An ever-present red clay.
- (c) Silica, either as chert, chalcedony, or quartz, universally associated with barite. The well known blossom of Washington County consists of chalcedony in thin bands, coated with quartz.
- (d) Limonite, which occurs as large and small masses, sometimes internally intergrown with the barite.
- (e) Galena, which is also sometimes intergrown with masses of barite.
- (f) Marcasite and Pyrite: these minerals sometimes remain as unaltered nuclei at the center of limonite, but are not common because most of the deposits are so completely oxidized.

All of the commercially important barite occurs irregularly distributed through the deep red residual clays from the weathering of the Potosi and Eminence formations. The residual clays in which

the barite chiefly occurs very irregularly in depth from a few inches to many feet, as is usual with residual deposits; and commercial barite is encountered from as shallow depths as grass roots right down to bed rock. The depth of mining rarely exceeds 20 feet.

In size, the particles vary from minute grains to masses of several hundred pounds weight. However, the fragments recovered are from 1 or 2 up to 8 or 10 inches in diameter, and much of the finer material is lost.

The distribution of barite in clay is usually erratic; richer pockets, or streaks, sometimes termed leads, alternating with lean material. This represents more active aggregation of barite at certain points of emergence of underground water channels.

At least four possible theories might be advanced to explain the origin of the barite in dolomite¹. They are: (a) descending cold solutions; (b) ascending cold solutions under artesian head; (c) ascending hot solutions from deep-seated hidden igneous sources; and (d) original deposition in colloidal form, along with the disseminated silica, from sea water.

¹DAKE, C.L. "Potosi and Edgehill Quadrangle", Missouri Bureau of Geology and Mines. Vol. XXIII 2nd. Series 1930. p.204.

METHODS OF MINING BARITE IN MISSOURI.

The very shallow depth and wide distribution of the barite deposits in Missouri has resulted in extremely simple mining methods. Most of the recovery has come from shallow, open pits, closely spaced. The digging is done by hand with pick and shovel and the fragments of barite are picked up by hand. This method is known as "Gophering", or "Gopher-holing".

In the deep pits, a hand windlass and bucket are commonly used. The deeper pits are often enlarged or undercut at the base; and, in those deposits that show definite leads, short drifts are sometimes driven. When caving begins, the shaft is usually abandoned, though rough timbering is sometimes employed.

The present trend in the industry is towards mechanization. There has been a gradual decrease in the amount of hand mining and somewhat more than a corresponding increase in mechanical mining during the last few years. Power shovels are now being used for loading; and logwashers, crushers and jigs for cleaning and concentrating. By the mechanization process, ground that has already been worked by hand may be reworked and much finely broken barite, lost in hand mining, can be recovered. The larger scale operations resulting from mechanization, also permit the working of lower grade deposits, which the hand miner cannot handle. The mechanical mining and washing method will be appreciated, when it is recalled that less than 35 per cent of the ore is now recovered by the hand method.

Dr. G.A. Muilenburg has mentioned that there is a great need for a small, portable type of washer and concentrator that may be moved from place to place and used to wash dumps and refuse from abandoned hand mines and other small deposits.

MILLING METHOD OF BARITE IN MISSOURI.

In the earlier operations, hand cleaning was employed. In this method, the material is allowed to thoroughly dry, as a result of which, some of the clay falls off. The larger lumps are then cleaned with a hatchet or hammer, the smaller, dumped in a "recker" or "rattler" and violently agitated until much of the clay is jarred loose. Many of the rockers have a coarse screen bottom, so that the clay and fine barite drop out. Others must be dumped. Small, portable jigs and log washers are now used.

It is important to note that barite can be separated from Calcite by the flotation method^{2,3}. The metal salt-silicate combination retards the calcite without affecting the barite. The pulp is conditioned with copper sulphate before the silicate is added. Oleic acid and sodium oleates are used to float the barite.

2

Dean, Clemmer, Cooke: "Use of Wetting Agents in Flotation" R.I. 3333
Feb. 1937.

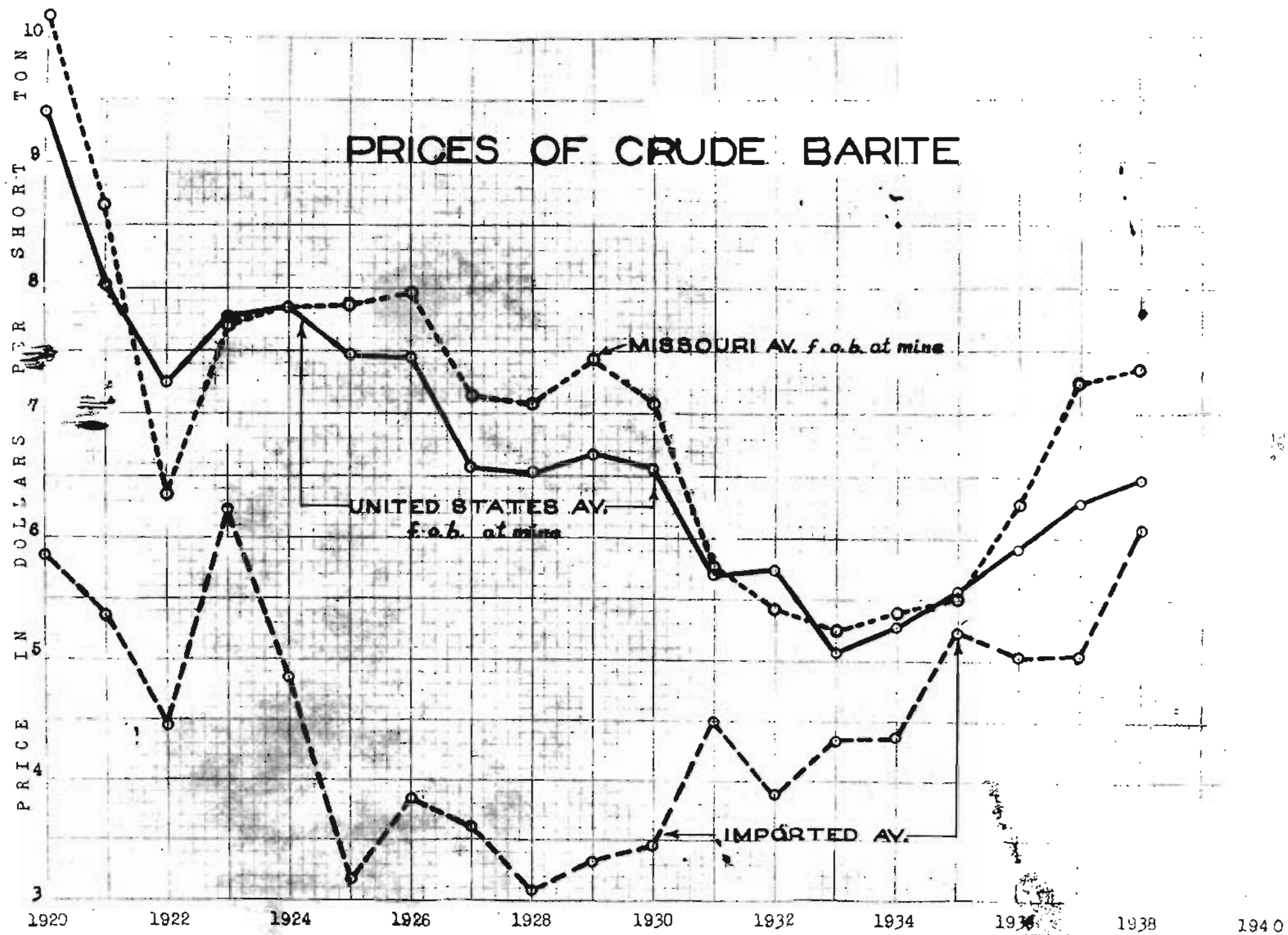
3

Coghill, DeVaney, Clemmer and O'Meara: "Flotation and Depression of Non-sulphide: Calcite, Silica and Silicate, Fluorspar, Barite, Apatite, and Tungsten Minerals". R.I. 3239, U.S. Bureau of Mines, June, 1934.

Prices of Crude Barite, 1920-1938.*

Period	Average U. S. price, short ton	Average price imported, short ton	Average Missouri price, short ton
1920	\$ 9.39	\$ 5.85	\$ 10.17
1921	8.02	5.36	8.65
1922	7.25	4.47	6.35
1923	7.77	6.23	7.70
1924	7.85	4.85	7.83
1925	7.47	3.17	7.87
1926	7.45	3.82	7.96
1927	6.57	3.60	7.15
1928	6.51	3.09	7.09
1929	6.67	3.32	7.12
1930	6.55	3.45	7.08
1931	5.70	4.50	5.77
1932	5.74	3.89	5.42
1933	5.08	4.34	5.25
1934	5.29	4.37	5.40
1935	5.56	5.23	5.52
1936	5.91	5.03	6.28
1937	6.30	5.03	7.23
1938	6.47	6.09	7.36

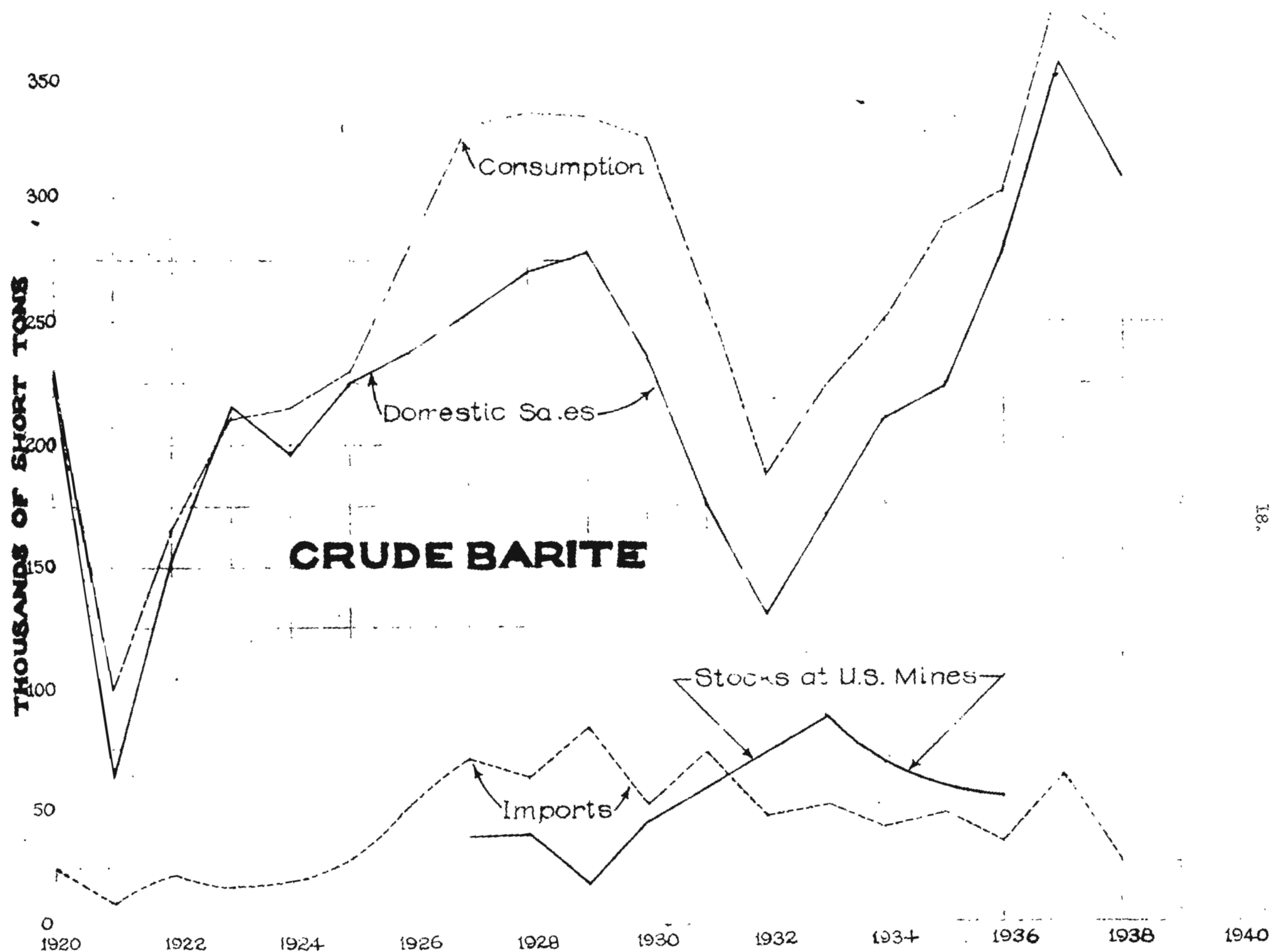
- *U. S. Bureau of Mines data from (1) Minerals Yearbook, 1932-1939.
 (Articles on "Barite and Barium Products" appearing in these issues).
 (2) The Mineral Industry, edited by G. A. Roush (McGraw-Hill), vols.
 35-38, and 40-46.



UNITED STATES: (1) Consumption
 (2) Domestic Sales
 (3) Imports
 (4) Stocks at mines) of CRUDE BARITE,
 in short tons*

Year	Consumption	Domestic sales	Imports	Stocks at U. S. mines, Dec. 31st
1920	229,443	224,500	25,000	
1921	100,607	66,369	10,200	
1922	167,842	155,040	21,900	
1923	210,587	214,183	17,000	
1924	213,163	196,332	21,550	
1925	232,685	228,063	28,650	
1926	281,056	237,875	49,800	
1927	330,190	254,265	70,400	37,000
1928	334,695	269,544	61,765	38,000
1929	334,406	277,269	55,729	17,000
1930	325,195	234,962	52,111	44,200
1931	265,270	174,520	73,030	
1932	189,409	129,854	45,758	
1933	223,047	167,880	49,957	86,252
1934	250,476	209,850	40,031	67,071
1935	290,344	225,111	47,048	58,350
1936	303,449	283,160	33,843	52,500
1937	333,982	355,838	64,992	
1938	364,985	309,663	24,845	

*U. S. Bureau of Mines data from (1) Minerals Yearbook, 1932-1939, articles on "Barite and Barium Products."
 (2) The Mineral Industry, edited by G. A. Roush (McGraw-Hill) vols. 35-38- and 40-46.



UTILIZATION OF CRUDE BARITE.

Barite, in its early history, found use as an adulterant in foods. It became unpopular on this account and laws were passed in some countries forbidding its use in foods. It was first used as a paint pigment in America about 1850. In this connection it was simply regarded as an adulterant for white lead for a long time⁴. During later years, scientific investigation of the properties of barite proved it to be a legitimate paint ingredient, having advantages for certain important uses. Barite was primarily used as a pigment in mixed paints and as a base in the manufacture of lake pigments. About 1909, Lithopone - a mixture of zinc sulphide and barium sulphate, attained some prominence as a paint material and dominated the entire field of utilization.

Nearly 64 per cent of barite consumed in the United States during recent years has been used in the making of lithopone. However, this situation is now changing and recently more barite has been going into the product "ground barite", on account of the large demand for it in the oil well drilling business⁵. Ground barite is also used as a white pigment, filler and inert base. Barium chemical manufacturing was built up by the exigencies of the Great War and has advanced, since 1915, from a small industry to one of considerable magnitude.

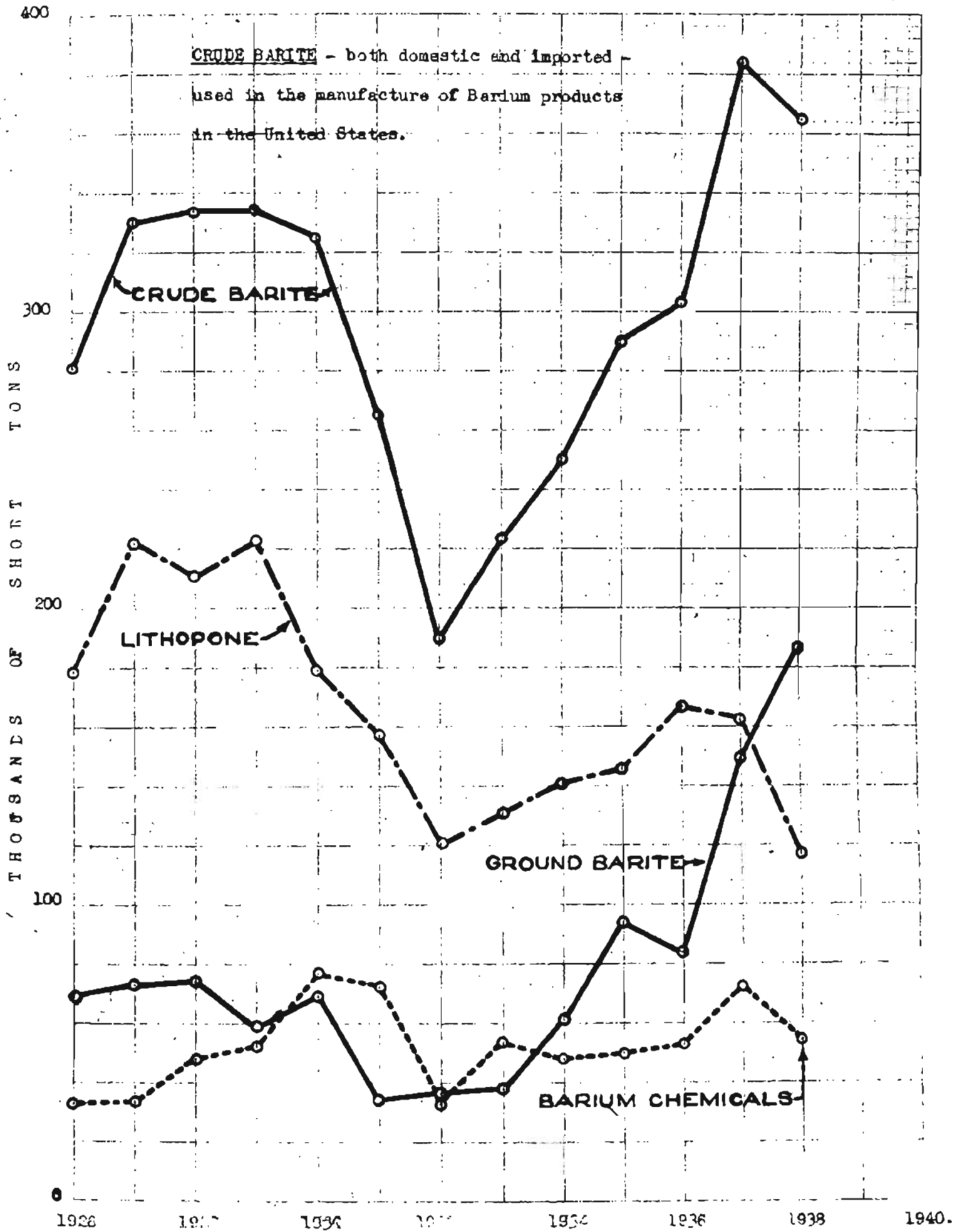
⁴
BOWLES, OLIVER and JUSTICE, C.W.: "Growth and Development of the Non-Metallic Mineral Industries" IC 6687, U.S.B. Mines. Feb., 1933. p.31

⁵
In 1938 186,607 short tons of barite went into ground barite, while 117,007 short tons went into lithopone.

Crude Barite (domestic and imported) used in the manufacture of barium products in the United States, in short tons.*

Year	Ground barite	Lithopons	Barium chemicals	Total
1926	69,043	178,889	33,119	281,056
1927	73,119	222,791	34,280	330,190
1928	74,814	211,592	48,289	334,695
1929	58,770	223,188	52,448	334,406
1930	69,426	178,944	76,825	325,195
1931	35,393	157,181	72,696	265,270
1932	38,026	131,761	53,260	223,047
1933	36,402	120,378	32,629	189,409
1934	61,123	140,734	48,619	250,476
1935	93,692	146,164	50,428	290,344
1936	83,990	167,014	52,445	303,449
1937	148,930	162,682	72,371	383,982
1938	186,607	117,007	54,250	364,985

* U. S. Bureau of Mines data copied from: (1) Minerals Yearbook (copies of 1932-1939); (2) The Mineral Industry, edited by G. A. Roush (McGraw-Hill), vols. 36-39 and 40-46.



Apart from the three main uses for Crude Barite, illustrated graphically, a finer distinction will be gone into in the ensuing pages. Separate chapters will be devoted to ground barite and lithopone and the various "barium chemicals" will be taken up separately.

II - GROUND BARITE

Preparation:- Ground barite is the crude ore after it has been washed, jigged, and ground very fine. Naturally, the process is varied somewhat in different plants according to the original condition of the ore. The general practice, however, is to crush the ore to about 1 inch and then remove the clay and earthy material by log washing. Often this washing is done at the mine; hence, need not be repeated at the grinding mill. The next step is to grind the cleaned material, usually in tube mills; then the ground barite, suspended in water, is either screened or water-floated in order to remove any coarse particles. If off-color, sulphuric acid is used to bleach the stains due to oxides of iron, out of the finally ground barite. After being washed several times with water, the bleached product is dried, pulverized, and packed in bags or barrels. The dominant position held by Missouri in the ground barite industry is due to the grade and texture of the ore, which is soft and easy to grind, as compared with the hard, crystalline variety found in other sections of the country.

Uses:- Ground barite is used principally as a heavy medium in mud in the drilling of deep oil wells where high gas pressures are encountered. This use took nearly 80 per cent of the total sales of ground barite in 1938; and was the reason why more barite ore went into producing ground barite than lithopone for the first time in the United States' industry. No other single use took over 5 per cent of the total sales during that year. The other main use of the material is as a filler - due to its being extremely heavy, chemically inert and white.

The paint, paper, rubber, linoleum and cloth industries all use ground barite to add weight and body to their products.

The tonnages and per cent of total Ground, or Refined Barite sold or used by producers in 1938, by consuming industries was as follows:-⁶

Industry	Short tons.	Per cent of Total.
Well drilling	126,697	79.
Paint	8,227	5.
Glass	7,963 ⁷ .	5
Rubber	2,844	2
Other ⁸	13,576	8
Not reported	2,615	1
	⁷ 161,422	100.

⁶
Minerals Yearbook, 1939. U.S. Dept. of Interior. p.1327.

⁷
Includes some crushed barite used in the glass industry.

⁸
Includes barite used in making paper, oilcloth, linoleum, cloth and sugar, as well as minor quantities used in other industries.

In former years it was estimated that from 50 to 70 per cent of ground barite was consumed in the paper and rubber industries.

As a rubber filler, bleached or unbleached, ground barite is employed where a soft rubber article is desired, as in rubber bands, tubing and the like; but not where strength and resistance to abrasion is required, as in auto tires.

The bleached form is used in papers where weight is desirable with a high finish, as in Bristol board, playing cards, and plate paper. Natural barite is not often used in high grade paints, but a limited quantity is employed in the cheaper grades and the bleached mineral is used directly as an extender and loader and as a base for lake colors.

Ground barite does not possess satisfactory covering power when applied in making paint, unless it is very finely divided. Inferior qualities of lithopone sometimes contain natural barite, which reduces the capacity and covering power and causes them to give a yellow-white tint when in linoleum. The natural mineral may be detected by means of a microscope - the precipitated barium sulphate appearing as a fine powder composed of minute crystals of uniform size.

Finely ground barite mixed with a colloidal clay, such as bentonite, and a suitable suspending medium, is effective in making up heavy liquids, used as a seal in drilling for oil and gasses.

Unbleached ground barite is used in molded goods, such as buttons and rubber articles. One of its newer uses, in the molded hard rubber industry, is as a component part of the protecting hard rubber shield around X-Ray tubes. Because of its high density, ground barite tends to absorb the rays and thereby protect the

operator, excepting where the shield is open. Plaster containing a large percentage of ground barite is used on walls of X-Ray rooms in order to limit the radiation of the rays. It is also used in making brick for the construction of X-Ray laboratories, replacing, in both cases, the lining of sheet lead used to prevent the rays from escaping and doing possible injury.

Ground barite is also used in the manufacture of artificial ivory.

As previously mentioned, its most important use - that use which consumed 79 per cent of its total tonnage in 1938 and which placed it ahead of lithopone in consumed tonnage for the first time in history - is that of a heavy medium in the mud used in drilling deep oil wells where high gas pressures are encountered.

GROUND BARITE IN DRILLING DEEP OIL AND GAS WELLS.

In rotary drilling, the efficiency depends to a large degree on the proper functioning of the circulatory system. Continuous removal of the material loosened by the drill prevents accumulation of the drill cuttings and freezing of the drill stem. Deposition of clay on the walls of the well and within the pores of the wall rocks minimizes the tendency of the wall to cave, while lubricating the drill pipe and reducing frictional power loss.

This clay deposition also acts as a seal and prevents loss of fluid into very porous, low-pressure formations, so that the circulation of drill cuttings to the surface will not be interrupted. It also seals off high-pressure gas and water-yielding horizons so that fluids from them cannot enter the well, causing "blow outs".

The fluid medium is usually a clay-laden fluid. Various chemical reagents are sometimes added to the mud fluid to develop special properties useful in sealing very permeable formations. Sodium aluminate is the base of one such chemical reagent marketed for this purpose. One part of this reagent is used with 600 parts of mud fluid by volume. Hydraulic lime, caustic soda, soda ash, and sodium silicate are also used for this purpose. The alkaline reagents react with clay forming gelatinous precipitates which accumulate on the surfaces of the clay particles, causing them to adhere.

Effective application of the circulating fluid in controlling high pressure gas, oil and water encountered in drilling, depends not only on its ability to seal the pores of the rock, but also upon the resisting hydrostatic pressure that can be developed to prevent extraneous fluids from entering the well. Here density of the fluid is important, the hydrostatic head at any depth increasing directly with the specific gravity of the fluid.

Mud fluids are capable of developing hydrostatic pressures as high as 0.59 pounds per foot of depth (85 pounds per cubic foot, as against 62.5 for plain water). This is sufficient to offset the high pressures ordinarily encountered in drilling; but, in abnormally high gas pressures, a heavier fluid is required. Finely ground barite, siderite or hematite can be used to develop hydrostatic pressures as great as 0.94 pounds per foot of depth (135 pounds per cubic foot, or somewhat over twice that of plain water). In such cases, too, the viscosity is such that the fluid can be readily handled by pumps. In practice, the actual maximum hydrostatic pressures found necessary are about 0.7 pounds per foot of depth.

Ordinary clay has a specific gravity ranging from 2.0 to 2.7, depending on its composition and condition; that of barite is 4.2, while hematite has a specific gravity of 5.2. Though of lower density than hematite, barite is generally preferred as a weighing material to hematite. Some varieties of hematite are gritty, causing rapid abrasion of pump liners, swivel and drill pipe, and the material promotes oxidation of any iron or steel with which it comes into contact.

Finely ground barite, prepared for use as a mud-weighing material and containing about 5 per cent of Aquagel is marketed under the name BAROID. Anything up to 95 pounds of BAROID may be added to each cubic foot of fluid, depending upon the amount of clay present and the density desired.

Heavy minerals must be ground so that upward of 90 per cent will pass a 200 mesh screen, and some authorities maintain that it is preferable if a large percentage will pass through a 300 mesh. If too coarse, the material tends to settle rapidly when the fluid is at rest.

If a high-pressure gas sand is being penetrated by the drill and there is not sufficient hydrostatic pressure developed in the well to offset the gas pressure, it will tend to enter and flow to the surface occluded in the mud fluid. In this way, the gas escapes in a finely divided mass of bubbles, expanding to form a froth as the fluid approaches the surface and is discharged. As a result, the gas pressure is gradually relieved and, sometimes, the escaping gas will expel the fluid at the surface.

PRICE:- The price of ground barite has been remarkably stable over the last decade - especially when the great depression of 1929-1932 and

succeeding industrial recessions are taken into account. The ordinary domestic grade, ("floated", in barrels, c.l. St. Louis) has fluctuated in the narrow range of \$23 to \$25 per short ton during the decade 1930-1940. Its current (1940) quotation is the \$25 figure. In this same period the imported German ground barite moved between the same limits, while the Italian stood constant at \$30 per ton. During 1940 there have been no quotations on either German or Italian ground barite, due to the war and other factors.

Market Areas in the U.S.A. The bulk of ground barite is consumed by the St. Louis-Chicago area and the Atlantic seaboard States. About 50 per cent of the ground barite consumed in the East normally comes from Missouri and (before the war) the balance was obtained partly from the Southern field and partly from imports (chiefly from Germany).

The chief rubber fabricators who use ground barite as a filler in rubber products are located in and around Akron, Ohio, and in the vicinity of New York City. Most of this barite comes from Missouri.

The paint industry is more spread out than the rubber industry and includes Michigan, Illinois, and Indiana in the mid-western market. A greater proportion of Southern ore finds its way into the paint industry, although Missouri still furnishes the larger part of its ground barite requirements.

LITHOPONE

The most important single chemical product made from barite is Lithopone — exceeded in tonnage by ground barite production in 1938, but never in value. The value of lithopone consumed in the United States in 1938 was \$9,975,012.00. It is an intimate mixture of zinc sulphide and barium sulphate, commonly containing approximately 70 per cent barium sulphate and 30 per cent zinc sulphide. It is not prepared by merely mixing the correct proportions of zinc sulphide and barium sulphate, but by the coprecipitation by double decomposition of solutions of barium sulphide and zinc sulphate. This is necessary because the particles produced in this fashion have certain desirable optical properties not possessed by the ordinarily finely divided barium sulphate and zinc sulphide.

Manufacture: — The basic raw materials necessary for the manufacture of lithopone are crude barite; coal, coke, or petroleum breeze; zinc, and sulphuric acid. Other chemicals, such as ferric oxide, alumina, lime and magnesia are required, but in minor quantities. A flow sheet for the manufacture of lithopone is shown on the accompanying page.

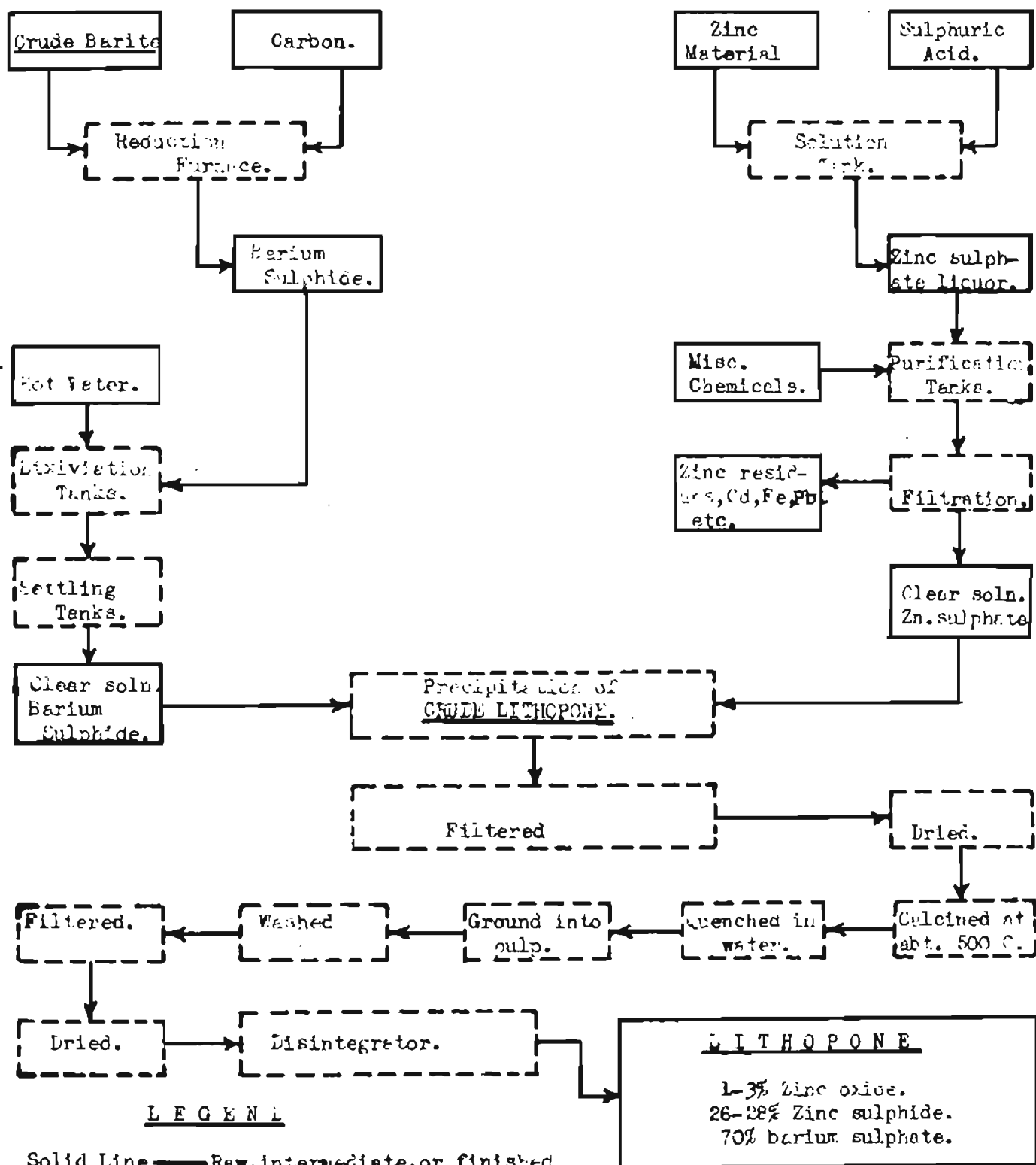
A necessary preliminary in the making of lithopone is the preparation of barium sulphide solution and a zinc sulphate solution. For the preparation of the former, the crude barite is first crushed and mixed with pulverized coal or other forms of carbon. In general, one part of coal to four parts of barite by weight is used. The mixture is heated for about four hours at

700 to 800° C. in a rotary furnace, the barium sulphate being reduced to barium sulphide. Molinari⁹ believes that the normal reaction under these circumstances is: $\text{BaSO}_4 + 2\text{C} = \text{BaS} + 2\text{CO}_2$, while at a slightly more elevated temperature it changes to: $\text{BaSO}_4 + 4\text{C} = \text{BaS} + 4\text{CO}$. In any event, the crude sulphide ("black ash") which contains about 70 per cent barium sulphide is then treated with hot water, and the resulting solution of barium sulphide is clarified. As it is essential to the quality of the pigment that this should be as pure as possible, and in particular free from iron and cadmium, the raw material used should be carefully selected, and the solution treated to remove any impurities. In modern practice, the reduction is generally carried out in a continuous rotary furnace, similar to that used for Portland cement.

In lithopone manufacture, it is also necessary that the zinc sulphate used shall be entirely free from traces of other metallic salt. Many processes have been patented for this purpose, such as treatment of the solution with bleaching powder to oxidize traces of iron salts to ferric hydroxide. Another method which is considered to give complete purity is to treat the solution with ammonia and warm it in order to precipitate the iron group as hydroxides. The hot solution is then treated with pure metallic zinc, which throws out copper, thallium, nickel, and finally cobalt by electrolytic action. The zinc sulphate solution is prepared by

⁹Molinari, Dr. Ettore, "General and Industrial Inorganic Chemistry;" P. Blakiston's Son & Co., Philadelphia (1920).

FLOW SHEET OF MFG. OF LITHOPONE



dissolving zinc in the form of zinc ash, scrap, skimmings, slab zinc or roasted ore in dilute sulphuric acid. The resulting solution is then purified by the precipitation method mentioned above.

The precipitation of the pigment is effected by running the barium sulphide solution into a vat and adding the zinc sulphate slowly with constant stirring, until it is in slight excess. The precipitate formed is collected and washed in the usual manner and dried at a low temperature to avoid oxidation of the zinc sulphide. The material in this state forms a very indifferent pigment, and the great feature of Orr's invention was the subsequent process by which the pigmentary properties are developed. This consists of charging the dried precipitate into closed retorts, which are heated to a bright redness (700 to 800° C.), care being taken to exclude an excess of air. While red hot, the contents of the retorts are discharged into cold water. The pigment is then thoroughly ground while wet and filter-pressed and dried once more. The equation of the precipitation of lithopone is



Although the process is simple in theory, the production of a high-grade lithopone is not easy, first to ensure the absolute purity of the reagents; secondly, to control the calcination. The function of this latter is to convert both the zinc sulphide and the barium sulphate from the amorphous to the crypto-crystalline condition, and to form an intimate combination between the two (ZnS.BaSO_4). This results in a considerable increase of refractive index, and consequently opacity, in the product; but, if it is

carried too far the pigment becomes coarse and gritty, owing to an increase in the size of the particles and development of crystalline shape. The essence of the operation is to alter the internal structure of the particles whilst retaining their amorphous structure. It is also essential to prevent oxidation of the product during calcination and whilst transferring the product to the water, as any material content of zinc oxide impairs the opacity and inertness of the pigment.

Finally the grinding of the lithopone presents considerable mechanical difficulty as the final product must be completed as closely as possible with zinc oxide in texture. The removal of the coarse and intermediate particles formed during the calcination, without unduly raising the cost, is not an easy matter.

The grade of lithopone is dependent on purity, fineness, whiteness, resistance to light, opacity and uniformity.

Composition of Lithopone

According to the equation $\text{ZnS} \cdot \text{BaSO}_4$, the barium sulphate and zinc sulphide should be in equal molecular proportions; which is equivalent to 29.5 per cent zinc sulphide and 70.5 per cent of barium sulphate. In actual practice the composition approximates the following figures:

Barium sulphate	67.43 to 75.41 percent
Zinc sulphide	23.10 to 29.36
Zinc oxide	0.30 to 2.96
Soluble salts and impurities	0.08 to 1.50
Moisture	0.06 to 0.35

The small proportion of zinc oxide is normally present, owing to slight oxidation during manufacture. However, it should not exceed two per cent. For some purposes, such as grinding with acid varnishes, even a trace of zinc oxide is detrimental. For such purposes the zinc oxide is extracted by quenching in dilute acetic acid instead of plain water.

While 30 per cent of zinc sulphide is the standard grade, qualities containing a lower proportion of zinc sulphide are made for the sake of their cheapness. Some lithopone contains as low as 15 per cent of zinc sulphide. This grade is reduced by mechanical mixture with blanc fixe. A "double strength" lithopone, containing 60 per cent zinc sulphide has also been introduced. Although this possesses abnormally high opacity, the high proportion of zinc sulphide renders it very susceptible to oxidation on exposure. In Germany it is a standard practice to prepare the lithopone in this strength and to reduce it to the standard 30 per cent by mechanical mixture with crystalline barytes, in order to obtain a low oil absorption.

Again, Dr. Molinari¹⁰, the Italian authority, regards lithopone as a variable mixture of zinc sulphide and barium sulphate of much wider limits. He places the percentage of zinc sulphide as from 11 to 42 per cent. He calls "lithopone" containing 11 to 18 per cent zinc sulphide the yellow (tinted) variety; 22 to 30 per cent blue; and 32 to 42 per cent green.

¹⁰See Footnote 9, shown on Page 31.

It is roughly true to say, other things being equal, that the price of lithopone increases with increased per cent of zinc sulphide present.

Constitution of Lithopone

There is no doubt that some form of combination, probably of a semi-molecular, crystal lattice type, takes place between barium sulphate and zinc sulphide during the calcination process in the making of lithopone. This results in the opacity of the mixture being greater than that of a mechanical mixture of the two constituents. The exact constitution produced is not yet exactly understood, but it is quite certain that the combination is a better pigment than either compound taken alone. Thus, the barium sulphate must be considered as an essential constituent, and not an adulterant.

Uses of Lithopone

Lithopone was not produced in the United States prior to 1906. Its use has grown tremendously as a pigment in paints, rubber goods, paper, oilcloth, and window shade cloth. Lithopone possesses an excellent "dovering power" and other advantages over white lead in paint. It is not poisonous and is not blackened by hydrogen sulphide, ammonia sulphide, or other sulphur fumes, which convert the white lead ($2\text{Pb}(\text{OH})_2 \cdot \text{PbCO}_3$) of lead paint into black lead sulphides:

$$(2\text{Pb}(\text{OH})_2 \cdot \text{PbCO}_3) + 3 \text{H}_2\text{S} = 3\text{PbS} + 4\text{H}_2\text{O} + \text{H}_2\text{CO}_3.$$

However, it must be noted that lithopone possesses the characteristic of darkening on exposure to sunlight and regaining its color in the dark. Manufacturers have succeeded in overcoming this defect. This discoloration is due to the zinc sulphide reacting with traces of impurity in the way of compounds of foreign metals, of which lead, thallium and manganese are the most active, with the formation of colored sulphides. This action is stimulated by light, while in the dark it is reversed, owing to the oxidation of sulphides in the presence of air. Chemically pure zinc sulphide is immune from this defect. According to this, the secret of the production of light fast lithopone lies in the complete purification of the reacting solutions. In practice, however, the action is prevented by adding small quantities of alkaline earths, notably magnesium oxide; and light fast lithopones always show a distinctly alkaline reaction. According to a patent taken out by the New Jersey Zinc Co. in 1922, the necessary slight alkalinity is obtained by keeping the barium sulphide in slight excess in the precipitation. The alkalinity should lie between such limits that 100 grams of pigment require not less than 10, or more than 20 cc. of N/50 sulphuric acid for neutralization.

In 1920, after considerable research, a lithopone pigment was produced which was sufficiently resistant to sunlight and moisture to permit its use in both interior and exterior used paints.

For exterior use lithopone must be mixed with other white pigments, such as zinc oxide (lead free) and some inert substances, such as magnesium silicate or silica, together with the proper oil and driers.

A recommended composition for external use consists of the following:

Lithopone	45 per cent
Zinc oxide	40
Inert material	15

A paint of this type ready to apply contains about 62 per cent of pigment and 38 per cent of vehicles (oil and thinner) and weighs approximately 15 pounds to the gallon.

The following is a commercial specification of lithopone for use in paint:

(1) Composition: - To contain a minimum of 99 per cent of calcined co-precipitated barium sulphate and zinc sulphide.

Zinc sulphide	26 to 32 per cent
Zinc oxide	not exceeding 2 per cent
Barium sulphate	Balance, to make not less than 99 per cent.

(2) Size of Particles: - Very fine (+300 mesh not to exceed 0.5 per cent)

(3) Oil absorption: - 12 to 20 per cent

(4) Volatile matter Not to exceed 0.5 per cent

(5) Water-soluble salts Not to exceed 0.5 per cent;
alkalinity not to exceed 0.1 per cent; calculated
as Na_2CO_3 .

Special Lithopones

Since 1933 a considerable market has arisen for "titanated" lithopone. This material is essentially a physical combination of titanium oxide and barium sulphate, in the same way in which ordinary lithopone is a combination of zinc sulphide and barium sulphate. The pigment was originally introduced on an industrial scale in 1914, but its development was retarded by the war, and it was not until 1921 that supplies became available in the United States. The main source of the titanium oxide used in making the material comes from the mineral ilmenite, or titaniferous iron ore, FeTiO_3 .

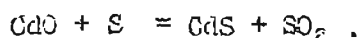
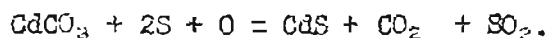
Cadmium Lithopone (or Cadmopone Yellows)

Cadmium yellow is the sulphide of the metal cadmium, with the formula CdS . Cadmium sulphide occurs naturally in small quantities as the mineral "Greenockite", but for use as a pigment it is always prepared artificially. There are three ways of preparing Cadmium yellow:

(1) Precipitation of a soluble salt of cadmium by hydrogen sulphide according to the reaction: $\text{CdCl}_2 + \text{H}_2\text{S} = \text{CdS} + 2\text{HCl}$. The principle of this reaction is followed in practice, but instead of passing sulphuretted hydrogen through the solution, it is often more convenient to acidify it with hydrochloric acid and add sodium sulphide. The great thing to be guarded against is the precipitation of sulphur in the free state with the pigment. When properly prepared, all the sulphur should be chemically combined with the cadmium as sulphide.

(2) Roasting cadmium carbonate or oxide with sulphur.

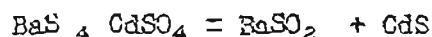
This method yields a pigment of good texture. The following are believed to be the reactions:



(3) Subliming a mixture of metallic cadmium and sulphur.

In this method the vapors of the two combine. The operation must be performed out of contact with air, otherwise the sulphur will burn to sulphur dioxide in preference to forming the cadmium sulphide. The product from this method is in an extremely fine state.

The CADMOPONE YELLOW, or cadmium lithopone, is then made by co-precipitation of the cadmium sulphide with barium sulphate in the same manner as ordinary lithopone. The reaction goes:



This reaction is followed by calcination to develop the pigimentary properties.

Consumption of Lithopone

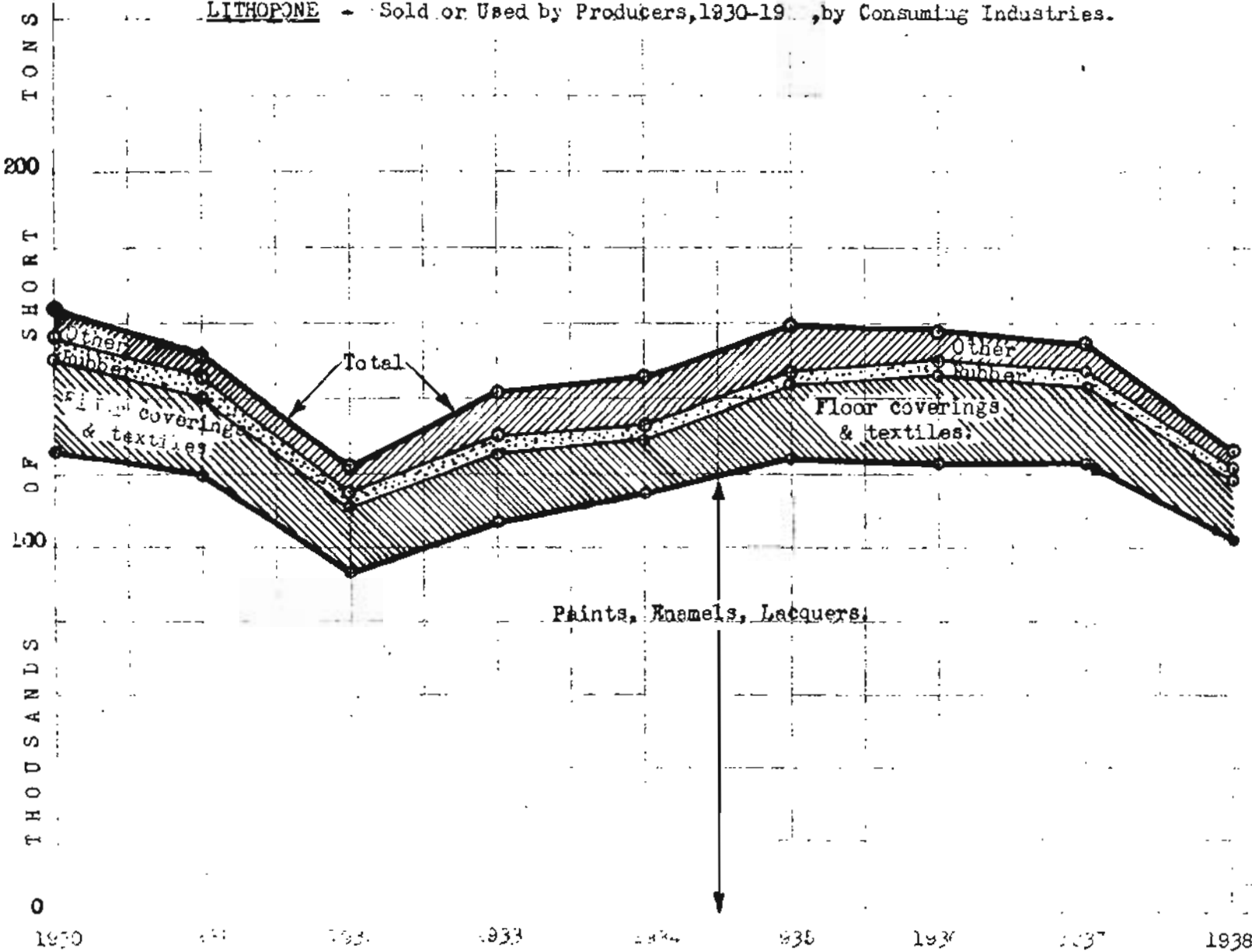
During the last decade the ratios in which lithopone have been consumed by various industries has been rather stable. Paints, enamels and lacquers have consumed from 76 to 81 per cent of the total from 1930 to 1938. In this same period, floor coverings and textiles used 10 to 15 per cent of the total; the rubber industry 2 to 4 per cent; and all others 4 to 8 percent. (See table and graph).

Lithopone: Sold or used by producers in the United States (1930-1938),
by consuming industries, in short tons.*

Year	Paints, enamels, lacquers	Per cent total	Floor coverings & textiles	Per cent total	Rubber	Per cent total	Other	Per cent total	Total
1930	126,076	76.8	23,656	14.4	5,997	3.7	8,336	5.1	164,065
1931	119,446	73.7	20,780	13.7	5,233	3.8	5,791	3.8	151,850
1932	93,465	76.8	17,601	14.5	3,955	3.2	6,646	5.5	121,667
1933	106,995	76.0	18,472	13.1	5,078	3.6	10,286	7.3	140,831
1934	114,472	78.6	14,811	10.2	4,596	3.2	11,636	8.0	145,565
1935	124,615	78.1	19,440	12.2	4,435	2.8	10,996	6.9	159,486
1936	122,461	77.3	23,085	14.6	4,908	3.1	7,865	5.0	158,319
1937	122,915	79.4	20,194	13.1	4,383	2.8	7,279	4.7	154,771
1938	101,924	81.1	15,400	12.2	3,143	2.5	5,274	4.2	125,746

*U. S. Bureau of Mines data taken from: (1) Minerals Yearbook, 1931-1939;
Articles on Barite and Barium Products. (2) The Mineral Industry, edited
by G. A. Roush (McGraw-Hill) vols. 50-40-46.

LITHOPONE - Sold or Used by Producers, 1930-1938, by Consuming Industries.



It will be noted that the divisions of the consumption of lithopone have been quite stable when compared on a percentage basis, in contrast to the wide change that has taken place in the standing of barite derivatives as a whole, in which ground barite displaced lithopone from first place (in tonnage) in 1938.

The main uses of lithopone, in order of tonnages consumed annually (year 1938) are as follows:

1. (a) Paints: (i) white pigment
(ii) inert body in colored paints
(b) Enamels: (i) white pigment
(ii) inert body in colored enamels
(c) Lacquers: (i) white pigment
(ii) inert body in colored lacquers

The above group consumed 101,924 short tons of lithopone in the United States in 1938, or 81.1 per cent of the total.

2. (a) Floor coverings }
(b) Textiles } 15,400 short tons, or 12.2 per cent
3. Rubber - 3,148 tons, or 2.5 per cent
4. (a) Preparation of barium chemicals }
(b) Making gramophone records } 5,274 tons, or
(c) Other uses } 4.2 per cent

The total lithopone consumed in the United States in 1938 was thus 125,746 short tons, valued at \$9,975,012.00.

Prices of Lithopone (During 1940 to date)

Following is a list of price ranges of the various grades of commercial lithopone during 1940:

(1)	Ordinary domestic class, delivered, in bags, per lb.	\$0.036 to 0.0385
(2)	" " in barrels "	.0385 - .0410
(3)	High strength, in bags, per lb.05 - .0525
(4)	" in barrels, "0525 - .055
(5)	Titanated grade, in bags, per lb.05 - .0525
(6)	" in barrels, "05 - .055
(7)	Cadmopone Yellow (Cadmium lithopone) per lb.45 - .55

BARIUM CHEMICALS

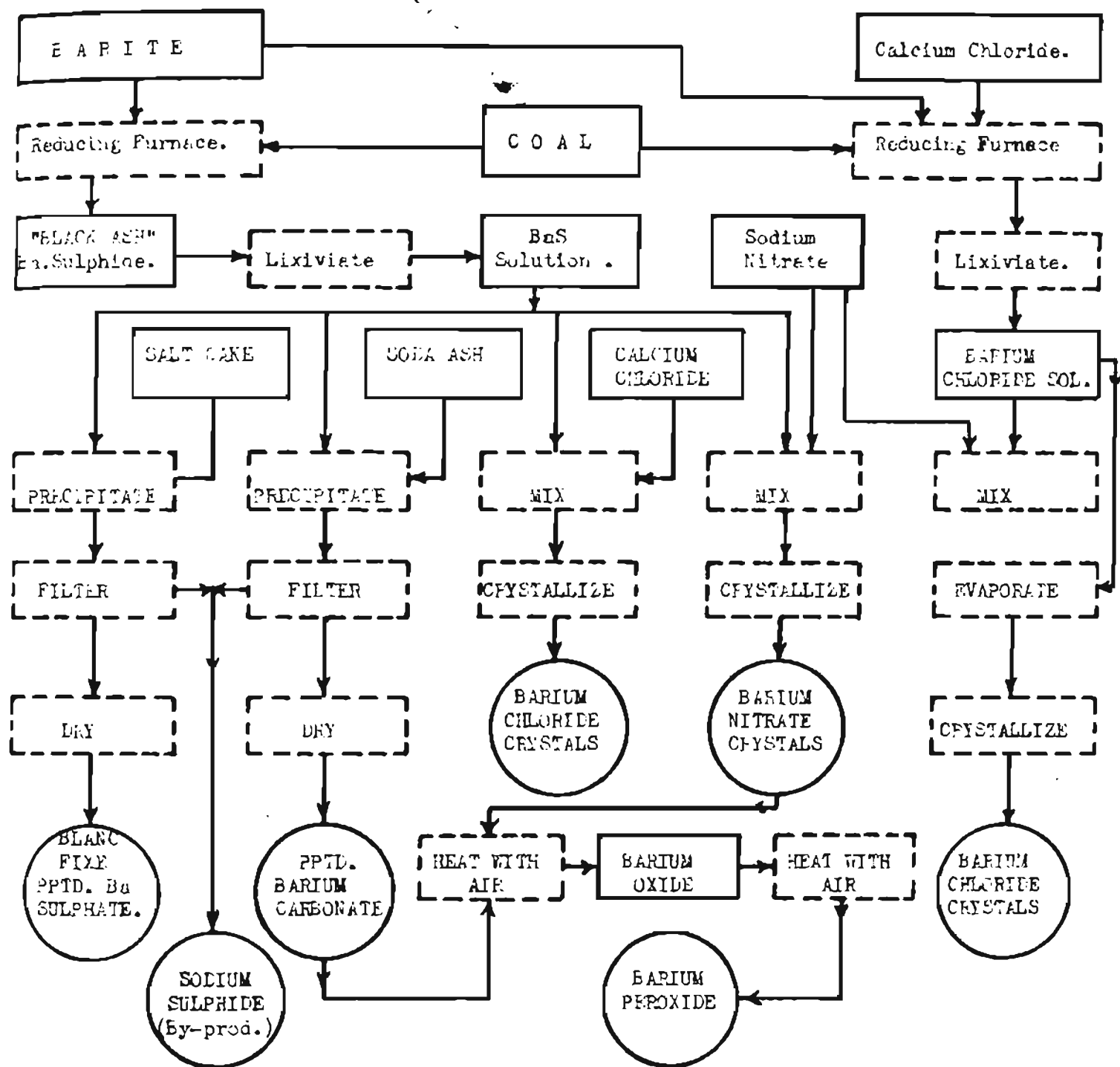
Barium Chemicals have important industrial uses in the United States. The most important of these are: Blanc fixe, or precipitated barium sulphate (which, although practically identical with ground barite chemically, has different physical properties), barium carbonate, chloride, nitrate, hydroxide and dioxide. Barium sulphide, which is prepared by heating a mixture of crude barite with one of the forms of carbon, is also of importance - but merely as the starting point in preparing other of the barium chemicals.

Both barite and witherite are used in the United States as the raw material for manufacturing barium chemicals, but the quantity of the latter used is relatively small and most of it is imported from England. The high grade barite of the soft type is preferred in making barium chemicals; but barite which cannot be used for preparing the highest grades of ground barite can be used.

Usually, barite is first changed to barium sulphide as an essential step in the making of barium chemicals. This is brought about by heating the barite with carbon in a furnace, or by fusing it with sodium carbonate.

The flow sheet shown is representative of a plant producing barium chemicals in general. These barium products, as well as others not shown in the flow sheet, will now be considered individually.

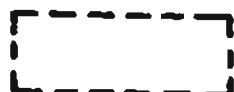
FLOW SHEET OF BARIUM CHEMICAL PLANT



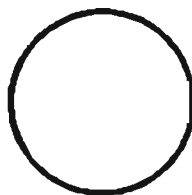
LEGEND



Raw materials, intermediate products.



Apparatus, or steps in process.



Finished Product.

BARIUM SULPHIDE.

Barium sulphide is obtained by heating a mixture of crushed crude barite and pulverized coal, or other forms of carbon, such as tar or oil, in a furnace. In general, one part of coal to four parts of barite by weight is used. The mixture is heated for about four hours at 700-800 C in a rotary furnace. The barium sulphate is thus reduced to barium sulphide. The normal reaction under these circumstances would seem to be:

$\text{BaSO}_4 + 2\text{C} = \text{BaS} + 2\text{CO}_2$, while at a slightly more elevated temperature it probably changes to:



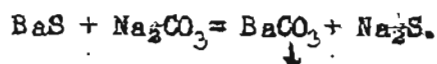
The crude sulphide produced ("black ash"), which contains 80 to 70 per cent barium sulphide, is then treated with hot water and the resulting solution of barium sulphide is clarified. Clarification can be effected by the addition of 1 or 2 per cent of caustic soda (at 36 Ba), the almost colorless sulphide crystallizing from the concentrated liquid.

USES: The important use for barium sulphide is as a stage in the preparation of other barium compounds (See Flow Sheets of Lithopone and Barium Chemical Plants). It is a starting point in the production of these compounds. By itself, it is of little other use. It has been used to replace barium hydroxide in the treatment of beet-sugar molasses; but since this whole process has fallen into disfavor, it can be said that it finds little use there either.

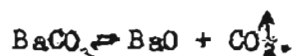
PRICE: Due to its intermediate nature in the manufacture of barium chemicals and lithopone, BaS is made at the plants direct from barite and is not a widely marketed product. It has no regular quotation.

BARIUM CARBONATE.

Preparation: Barium carbonate is precipitated from a solution of barium sulphide by sodium carbonate (soda ash) and sodium sulphide is obtained as a by-product.

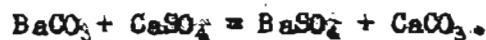


Barium carbonate occurs in nature as the mineral Witherite, which may be decomposed at a temperature of 1400 C as follows:



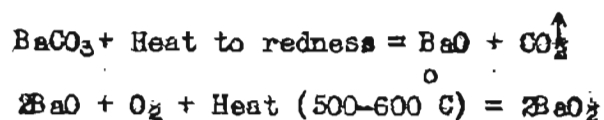
Barium carbonate can also be prepared by passing a current of carbon dioxide gas through a solution of barium sulphide.

USES: Barium carbonate is a white, insoluble salt, which finds its largest use in the ceramics industry, where it is employed to prevent scumming on the surface of clay products and for the manufacture of optical glass. Nearly all of the soluble salts which cause this scum are sulphates, and calcium sulphate is by far the most troublesome in this respect. If barium carbonate is added to a clay containing calcium sulphate, the products of the reaction will be barium sulphate and calcium carbonate. Both are relatively insoluble and will not form a scum.



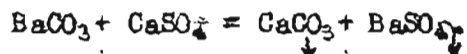
Barium carbonate is used in manufacturing of flat wall paints which produce a velvety finish. Witherite (natural barium carbonate) can not be used for this purpose and should not be confused with the precipitated product.

Barium carbonate is used as a raw material for making barium peroxide. Barium carbonate is first converted into barium oxide by heating it to redness in a closed apparatus. Then the oxide is converted to the peroxide by heating to about 500-600 C in a current of air free from carbon dioxide and moisture. The reactions can be shown by the equations:

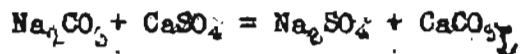


Water Softening and Treatment with Barium Carbonate.

Barium carbonate is also sometimes used to remove calcium sulphate from water. Barium carbonate has the formula BaCO_3 , and is practically insoluble in water free from CO_2 . In the presence of water containing CaSO_4 , however, barium carbonate reacts with calcium sulphate according to the following formula:



Sodium carbonate can also soften water and is cheaper than barium carbonate, but has the disadvantage of producing sodium sulphate as a by-product.



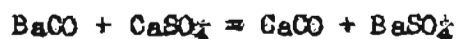
Sodium sulphate has a tendency to cause foaming in steam boilers unless the boiler be blown off frequently, while the insoluble CaCO_3 and BaSO_4 are precipitated during softening.

Hardness in water is due to the presence of bicarbonates, carbonates, sulphates, chlorides and nitrates of calcium and magnesium; also, to acid constituents. When a hard water, on being boiled, loses its bicarbonate it is called a temporary hard water. If the mineral acid, or some carbonates which can not be removed by boiling

are present, the water is known as permanent hard water. Total hardness is the sum of the two types of hardness.

There are various ways of expressing hardness. Perhaps, parts per million of CaCO_3 is preferable. German degrees designate parts of CaO in 100,000; while French degrees are parts of CaCO_3 per 100,000 parts of water.

There are many kinds of processes for water softening, but the most generally used ones are the "lime soda process" and the "barium process". In general, the plant for the barium process resembles that of the lime soda process. Barium is introduced through a funnel into an inner tank, where the raw water is brought in contact with the barium carbonate. CaCO_3 and Mg(OH)_2 are precipitated in an outer compartment and so do not prevent the proper mixing of the raw water with the barium carbonate. An automatic syphon is so arranged that the raw water can be fed to the settling tank intermittently, in order to produce a regularly recurring pulsation of the water in the settling tank. This has the effect of keeping the heavy barium carbonate in continual agitation and brings the barium carbonate into intimate contact with the raw water. The barium carbonate, while insoluble in pure water, is soluble in saline water (water containing calcium sulphate) in the proportion that the sulphate radical is present.



The efficiency of the barium softening process and its comparison with that of the lime soda softening process are shown in the following tables:-

Hardness	Parts per million	
	Raw water	Treated water
Total hardness	488	25.7
Temporary "	240	—
Permanent "	248	—

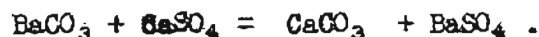
Substance	Parts per million		
	Raw water	Lime soda process	Lime barium process
Total residue	351.5	209.6	61.4
Mineral	286.9	—	—
Carbon dioxide	73.5	—	—
Silica	7.2	—	—
Oxide of iron and alumina	1.0	—	—
Magnesia	21.4	10.3	9.2
Lime	130.5	7.8	8.0
Soda	5.4	77.5	5.4
Sulphuric anhydride (SO ₃)	102.4	102.4	4.2
Nitric acid	Trace	—	—
Total hardness	285.5	39.3	37.5
Permanent hardness	167.7	—	—
Temporary hardness	117.8	—	—

The barium softening process thus has certain advantages over the lime soda process:

1. It has a higher softening power.
2. It can remove impurities from the raw water.
3. Sodium carbonate has the tendency to form foaming in a

boiler because of the presence of sodium sulphate in the water:

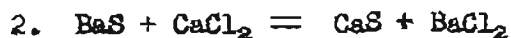
$\text{Na}_2\text{CO}_3 + \text{CaSO}_4 = \text{Na}_2\text{SO}_4 + \text{CaCO}_3$. Barium carbonate has not this ^{dis}ad-
vantage because both CaCO_3 and BaSO_4 are insoluble in water and
can be removed during softening:



BARIUM CHLORIDE

Barium chloride crystallizes in square plates of the rhombic system with $2\text{H}_2\text{O}$, and is not hygroscopic as are CaCl_2 and SrCl_2 . It loses its water of crystallization at 60°C . and then melts at about 800°C . At this melting point, in the presence of steam, it gives HCl .

It can be prepared from the carbonate (Witherite, BaCO_3) with HCl . However, the usual commercial preparation is from the sulphide BaS (see flow sheet), by heating with a metallic chloride such as CaCl_2 or FeCl_2 . By Kolb's method a mixture of 100 parts of barium sulphate, 36 parts of lean coal, and 68 parts of calcium chloride (in very concentrated solution) are heated in a furnace at 900°C . The chloride is then dissolved in hot water. The reaction may be represented in two stages, thus:

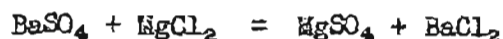


When calcium chloride is not available barium chloride is prepared by treating barium sulphide with a calculated quantity of hot dilute hydrochloric acid.

According to German Patent 257,277 (1911), if powdered barium carbonate is boiled and shaken for some hours with an excess of calcium or manganese chloride in concentrated solution, 95 per cent of the carbonate may be transformed into barium chloride which may be extracted from the mass by means of water as follows:



H. Kuhne proposed the manufacture of BaCl_2 by fusing barium sulphate directly with magnesium chloride:



However, the reaction is reversible so that the mass must be cooled rapidly. Magnesium sulphate then separates out as it is less soluble than BaCl_2 .

Uses

Barium chloride is largely used in the manufacture of blanc fixe (precipitated barium sulphate), lake colors, and as a mordant for fixing acid dyes on an inert base, such as aluminum hydroxide or blanc fixe. It is also used in the purification of salt; as a water softener for the prevention of boiler scale; as a chemical reagent for sulphur determinations; in the ceramics industry to some extent; in the manufacture of photographic chemicals; and in certain medicinal uses.

Price

There are two main grades of barium chloride marketed. The first is the domestic technical grade*, which has fluctuated from 3.1 to 5.1 cents per pound during the last decade (1930-40). The 1940 range has been 3.85 to 5.1 cents per pound.

The second is the chemically pure compound in crystalline form**, which has fluctuated from 13 to 25 cents per pound during the last decade, and at present (1940) has a consistent market at 25 cents per pound.

*Crystal form, in bags, c.l.

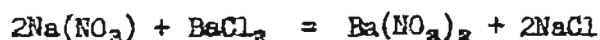
**Crystal form, in barrels.

BARIUM NITRATE

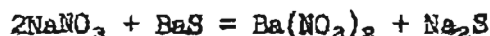
Barium nitrate is a soluble barium salt which is used principally for the manufacture of barium peroxide or dioxide. It forms shining octahedral crystals which are soluble to the extent of 7 parts in 100 in water. At a red heat it decomposes into BaO and nitrogen oxides.

Barium nitrate can be produced in the following four ways:

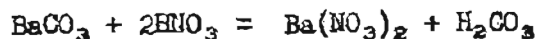
1. By adding sodium nitrate (Chile saltpeter) to a solution of barium chloride. The barium nitrate, which is comparatively insoluble separates on cooling:



2. By treating sodium nitrate with a solution of barium sulphide (see flow sheet):



3. By dissolving Witherite in a solution of nitric acid:



4. H. Kuhne has suggested fusing barium sulphate with twice the theoretical quantity of calcium nitrate:



When the mass is cooled and extracted with water, 75 per cent of the theoretical yield of barium nitrate is obtained.

Uses

The main use of barium nitrate is for making barium peroxide (or dioxide). It is used, too, in pyrotechnics for making green fire and green signal lights; and in making certain explosives. It has some medicinal uses similar to those of barium chloride.

Price

The price of barium nitrate has fluctuated during the decade 1930-40 between 7 and 10.5 cents per pound. The current price (1940) is from 8.5 to 10.5 cents per pound.

BARIUM SULPHATE (Blanc Fixe)

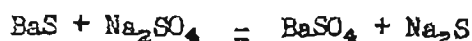
Precipitated barium sulphate, BaSO_4 , prepared in a barium chemical plant (see flow sheet), is the same substance chemically as barite, differing from it only in its physical condition. Barite is crystalline, the crystals being of the orthorhombic system, bipyramidal class. These crystals do not mix with particles of zinc sulphide to form an intimate contact mixture on account of their too great size, and it is hard and expensive to grind them sufficiently small and uniformly to fill the requirement. In low-grade paints, the irregular and non-uniform particles of barite can easily be detected under the microscope.

A better way of obtaining finely divided barium sulphate, useful for pigments, etc., than by resorting to grinding, lies in the precipitation of barium sulphate by chemical means. The product thus obtained has the distinctive commercial name of blanc fixe. The particles are of very fine and uniform size and of a relatively amorphous character. Blanc fixe can be made in the following four ways:



3. Blanc fixe ^{is} usually now made by precipitation of barium sulphate from a solution of barium sulphide by means of salt cake (sodium sulphate). (See flow sheet of Barium Chemical Plant). This method

produces a much denser product than that produced from barium chloride. In addition, sodium sulphide is yielded as a valuable by-product. The reaction is probably as follows



4. It can also be made as a by-product in the manufacture of hydrogen peroxide, when barium peroxide is treated with sulphuric acid:



Properties

Blanc fixe does not possess quite the same degree of chemical stability as natural barite, and although insoluble in dilute acids, is more readily dissolved on digestion with sulphuric acid. Unless carefully washed, it is liable to retain traces of acidity, and the grades produced as by-products frequently show a slight acid or alkaline reaction, and are also liable to contain traces of iron.

To obtain the precipitate in as fine a state of division as possible the reactions of any process listed above should be effected in the cold and with dilute solutions. Precipitation from hot and concentrated solution tends to the production of larger crystalline particles and consequent grittiness of the pigment.

The precipitated sulphate is allowed to settle, the supernatant water run off, and the pigment first washed by decantation and then filter-pressed and dried. The pulp from the filter press, containing about 25 per cent of water is used directly (to save the expenses of drying) for loading paper and fabrics and for use as a base for precipitating lakes.

Uses

Blanc fixe is more costly than natural barite but it is superior to it as a pigment and can be utilized for many purposes for which the coarseness of the natural product renders it unfit. Although it possesses more opacity than barite, owing to its fineness, it loses this entirely when mixed with oil. This renders it useless as a pigment in oil painting, which is unfortunate as its permanent qualities would make it invaluable. In water, on the other hand, blanc fixe possesses considerable opacity, and it is largely used as a water color by artists, under the names constant white, permanent white, process white, etc. It is particularly valuable for retouching of photographs for process reproduction, on account of its very pure colors.

Blanc fixe is also used extensively as a reagent for the precipitation of lakes and as a mineral base of the lake produced. It also finds use in lithographic inks. The battleship gray used by the United States Navy contains about 45 per cent of blanc fixe. Under the name of chemically pure barium sulphate it is used as an indicator in X-Ray photography.

Price

Blanc fixe is marketed in two forms: (1) As a dry powder and (2) as a pulp or paste containing 25 to 30 per cent water. The dry powder is used for ordinary pigments, and the pulp for loading paper and fabrics, for use as a base for precipitating lakes, and for making lithographic inks. The price of the dry powder* has fluctuated

*Blanc fixe: technical, X-Ray quality, in barrels.

between 9.5 and 13 cents per pound during the last decade (1930-40) and its present (1940) price has moved between 9.5 and 10 cents per pound. The market price of a blanc fixe pulp can always be calculated from the current dry powder market price by deducting the percentage of water present in the pulp.

BARIUM PEROXIDE

Barium peroxide (BaO_2) is obtained from the oxide by heating to about 500°C . in the presence of air. (See flow sheet of Barium Chemical Plant). At higher temperatures the peroxide loses oxygen. The crude product is a greenish mass but when pure it is a colorless powder, insoluble in water and forms hydrogen peroxide with dilute acids. On heating, it evolves oxygen. Barium peroxide, like other peroxides, such as hydrogen peroxide, contains the -O-O group, which is relatively unstable. This grouping explains the oxidizing and reducing power of peroxides in general.

Uses

The chief use of barium peroxide is as an oxidizing agent in the making of various chemicals, such as boric acid, glycol, sodium sulphate, etc. It is used also as a disinfectant, as a catalyst in the making of anthraquinone dye, as an oxygen carrier in electric cutting and welding, as a fuel, ingredient in explosives, a bleaching agent, as a process material in making synthetic caoutchouc (rubber), and as an ingredient in antiseptic soap powder.

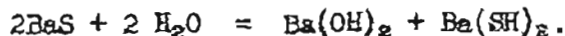
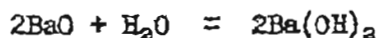
Price

In the last decade (1930-1940) the price of barium peroxide has fluctuated between 10 and 15 cents per pound. During 1940 it has also moved in exactly that range.

BARIUM HYDROXIDE

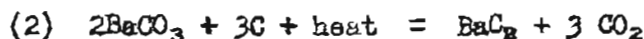
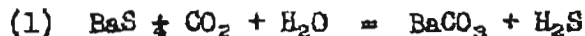
$\text{Ba}(\text{OH})_2$ is formed with the evolution of heat on dissolving the oxide in water. It is also obtained from the carbonate and from the sulphide, or by reducing the sulphate with carbon and treating the barium sulphide so formed with CuO - copper sulphide and barium oxide being thus produced. On lixiviating, the oxide dissolves to form barium hydroxide, and the copper sulphide is then reconverted into copper oxide. It has been observed that the copper sulphide easily retains much barium hydroxide, which is then transformed into carbonate or sulphate and renders the regeneration of the copper oxide difficult, so that it becomes necessary to decompose the copper sulphide by wet methods. The copper oxide may also be replaced by zinc oxide.

In the United States, $\text{Ba}(\text{OH})_2$ is obtained from barite by the Brandley and Jacobs process in which a ratio of four molecules of ~~BaO~~ BaSO_4 and five atoms of carbon in the form of coke is mixed in an electric furnace and heated. The product of this reaction contains 60 per cent BaO and 40 per cent BaS , while SO_2 is evolved. This product is leached with water and all the oxide and one-half of the sulphide are converted into the hydroxide:



From the hot solution the almost pure hydroxide (less than one per cent of impurity) crystallizes on cooling, while the mother liquor contains the barium hydrosulphide.

Barium hydroxide is also prepared by transforming the sulphide into carbonate by means of CO_2 and H_2O , and then preparing the carbide from it by heating with carbon in the electric furnace. With water, the carbide forms barium hydroxide and acetylene, which may also be utilized:



The hydroxide is soluble in water, forming a strongly alkaline liquid, and crystallizes with 8 H_2O , but loses 7 H_2O in the air, whereas the last molecule of water is expelled only at a dull red heat. At a white heat BaO is formed. It melts at 78°C . and fixes CO_2 easily from the air. One hundred parts of water dissolve 1.5 parts of the hydroxide at 0° , 2.9 at 15° , 11.75 at 50° , or 90.8 at 80° .*

Uses

The main use for barium hydroxide is the extraction of sugar from molasses and in the refining of beet sugar. As strontium or lime act in the same way and have less toxic, they have been largely substituted.

Price

In 1938 the market price for 500-pound barrels of barium hydroxide fluctuated between \$0.0475 and 0.055 ~~cents~~ per pound. This might seem surprising at first glance since the oxide from which it is derived had a market value of 9 to 11 cents per pound during the same period. However, it should be remembered that the commercial crystalline product is $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$. The anhydrous product was worth 15 to 17.5 cents per pound during the same period.

*Molinari, Dr. Ettore, Treatise on General and Industrial Chemistry; P. Blakiston's Son & Co., Philadelphia (1920).

BARIUM OXIDE

Barium oxide, BaO, is useful chiefly as the intermediate product in making barium peroxide, barium hydroxide and other barium salts. However, it also has a large number of scattered, small uses when used by itself, none of which consumes a large tonnage.

BaO was once obtained by heating barium nitrate or hydroxide to redness. Frank prepared it (German Patent 135,330) by mixing a barium salt, BaCO₃, with barium carbide and heating the mixture out of contact with air:

$$3\text{BaCO}_3 + \text{BaC}_2 = 4\text{BaO} + \text{CO}_2$$

To prepare the peroxide it is absolutely necessary to have a highly porous oxide. The decomposition of the carbonate by heat, $\text{BaCO}_3 = \text{BaO} + \text{CO}_2$, is reversible and gives a non-porous product; the reverse reaction may be prevented by the addition of carbon which reduces the CO₂ to CO, but the presence in the carbon of hydrogen or moisture must be avoided so that Ba (OH)₂ may not be formed. (W. Feld).

The porous oxide can be obtained by heating a mixture of barium carbonate and nitrate, containing a little hydrocarbon, to redness. At Niagara Falls, the oxide is obtained industrially in an electric furnace from a mixture of four molecules of BaSO₄ with five atoms of carbon in the form of coke (Brandley and Jacobs, German Patent 111,667). The product of the reaction contains 60 per cent BaO and 40 per cent BaS, while SO₂ is evolved. The oxide and sulphide are then transformed into barium hydroxide which has wide use.

The main use of barium oxide (as such, and not as an intermediate product in the manufacture of other barium chemicals) is as a drying agent. Porous barium oxide is, perhaps, the best all-round drying agent available for dehydrating gases, liquids and solids up to 1000° C. (See chart of comparison with other leading desiccators).

High-grade porous barium oxide, used as a drying agent, is manufactured by the low temperature reduction of pure barium carbonate. This process is protected by U. S. Patents 1,653,123, 1,913,289, 2,057,348, and 2,057,349. Barium oxide made by this process is claimed to be extremely reactive and porous and should not be confused with other grades of barium oxide prepared by electric furnace methods which are usually fused or semi-fused products entirely worthless for desiccating work.* Porous barium oxide should be kept in a sealed container out of contact with air containing carbon dioxide or moisture. Due care should be taken in handling it, as it reacts violently with water contact.

Prof. H. S. Booth of Western Reserve University was apparently the first to call attention to the use of porous barium oxide as a desiccant for laboratory work.** He states: "In a number of studies with gases being carried on in this laboratory barium oxide is being used most successfully to replace phosphorus pentoxide as a drying

*Properties and Uses of Porous Barium Oxide; Booklet issued by Barium and Chemicals, Inc., Willoughby, Ohio.

**Booth, H. S., and McIntyre; Jour. Ind. and Eng. Chem. (anal Ed.), vol. 2, no. 1, p. 12, Jan. 1930.

agent. Its freedom from stickiness and ease of handling quickly made it a favorite with the workers here. It should not be handled with moist or wet hands because the heat of reaction with the water may be enough to cause a burn. It can be handled with dry hands safely enough. As expansion occurs upon hydration, it should be mixed with glass wool or else left in lumps about 7 to 10 mm. in diameter to prevent choking of the tube.

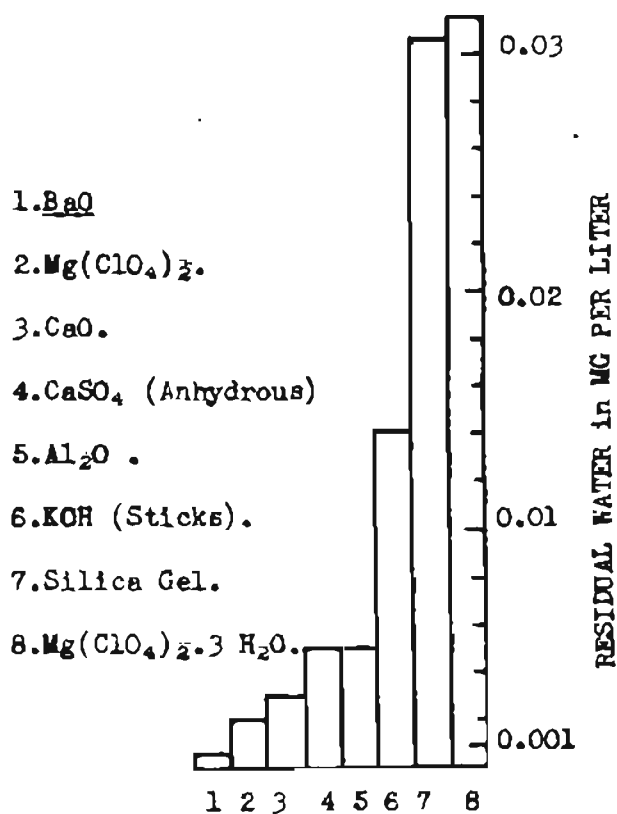
"We have found BaO especially valuable for drying such basic gases as ammonia, for which it is far superior to metallic sodium, as it yields no gas in its desiccating action.

"A preliminary study of the use of porous barium oxide in desiccators for analytical work has shown that the rate at which it removes moisture from the desiccator is the same as that of phosphorus pentoxide, and that it is far superior, not only in this respect but in many others, to either calcium chloride or sulphuric acid. We have therefore adopted it in place of other desiccants in the course in quantitative analysis. It is much cheaper than the calcium chloride sold for desiccators and is conveniently obtainable from the manufacturers in steel drums.

"The results of this study show that the porous barium oxide made by the low temperature reduction of barium carbonate by carbon fulfills the requirements for a good desiccant. Barium oxide made by this method has a high activity and large capacity, though the oxide cannot be reactivated. Being in a solid, porous form, it is easily handled, does not become sticky, and does not channel if the container is pro-

BARIUM OXIDE AS A DESICCATOR.

Graphical representation of its efficiency compared
with that of other leading desiccating agents .



U.S. Department of Commerce, Bureau of Standards, RESEARCH
PAPER RP649. Part of Bureau of Standards Journal of Research, Vol. 12,
February 1934. "COMPARATIVE EFFICIENCIES OF VARIOUS DEHYDRATING
AGENTS USED FOR DRYING GASES (A SURVEY OF COMMERCIAL DRYING AGENTS)".
By J.H. Bower.

perly filled, but, on the contrary, may choke up the tube unless room for expansion is left. On account of its granular nature, as compared to the fine particles of phosphorus pentoxide, barium oxide calls for larger drying tubes to accomplish the same drying rate, but the total efficiency is about the same or slightly better than for phosphorus pentoxide."

Barium oxide can be, and is, used in hospitals in the preparation of absolute alcohol. Dr. G. Frederick Smith* says: "The preparation of 99.4 per cent alcohol is accomplished with barium oxide using the theoretical quantity of reagent by refluxing less than one-fifth the time required for the preparation of alcohol of approximately the same strength using calcium oxide."

**

In using BaO as a desiccant, Booth and McIntyre state:

"When an alkaline drying agent is permissible, porous barium oxide is excellent, and is particularly valuable in determinations affected by carbon dioxide, such as gravimetric calcium. Since barium oxide swells considerably on absorbing moisture, the bottom of the desiccator should not be more than half full."

In connection with using porous BaO in the drying of biologicals, Ecker and Pillemer*** state: Since the success of the desiccant-

*Dr. G. Frederick Smith; Jour. Ind. and Eng. Chem. (anal. ed.), vol. 1, no. 2, p. 72, Apr. 15, 1929.

**Booth and McIntyre; Jour. Ind. and Eng. Chem. (anal. ed.), vol. 8, p. 148, Mar. 15, 1936.

***"An Inexpensive Method for the Dehydration and Preservation of Complement and other Biological Materials;" Amer. Jour. Pub. Health, vol. 28, no. 10, Oct. 1938

ing process depends upon a desiccant of great efficiency, porous (granular) barium oxide was selected. It takes up moisture with great rapidity and has no measurable vapor pressure, and the fact that it cannot be reactivated is offset by its cheapness and availability. Barium oxide does not become sticky and does not channel if the container is properly filled."

Commercial barium oxide forms a grayish-white mass, sometimes in translucent cubes; its density being 5.7. Its heat of formation from the elements is 124,240 cal.* At 2000° C. it is completely fused. It does not conduct electricity and absorbs moisture readily with strong heating.

Price**

During 1940 the price of barium oxide, shipped in drums, fluctuated between 9 and 15 cents per pound.

*Molinari, Dr. Ettore; Treatise on General and Industrial Inorganic Chemistry; P. Blakiston's Son & Co., Philadelphia, (1920).

**Oil, Paint, and Drug Reporter - weekly issues up to July, 1940.

BARIUM PLATINOCYANIDE

Barium platinocyanide ($\text{BaPt}(\text{CN})_{4.4} \text{H}_2\text{O}$) forms yellow monoclinic crystals which, when viewed in various directions, appear violet-blue or greenish yellow. It has the property of becoming fluorescent under the action of X-Rays and ultra-violet rays.

Uses

It is used in X-Ray photography by coating the projecting screen with it. The screen converts the invisible shorter waves to the longer light waves, which readily affect a photographic film.

LESSER KNOWN BARIUM CHEMICALS

- (1) Barium chlorate is used in pyrotechnics and dyeing.
- (2) *Barium Chromate is used as a yellow pigment, and in the barium chromate method of analysis for sulphur.
- (3) Barium manganate has been used as a green pigment.
- (4) Barium persulphate ($\text{BaS}_2\text{O}_8 + \text{H}_2\text{O}$) can be obtained by electrolyzing barium sulphate mixed with sulphuric acid.

Prices

Of the above chemicals only barium chlorate is used in sufficient quantities, commercially, to warrant a regular market quotation. Its price, in kegs, has varied between 13.75 cents and 25 cents per pound during the past decade (1930-40). Its current quotation (1940) has fluctuated between 20 and 25 cents per pound.

*C. W. Hinman; Amer. Jour. Sci., vol. 3, no. 14, 1877, p. 478;
J. D. Pennock and D. A. Morton, Jour. Amer. Chem. Soc., vol. 25,
1903, p. 1265; M. Holliger, Z. anal. Chem., vol. 29, 1910, p. 84.

MIXTURES OF BARIUM CHEMICALS

In the making of pressed or blown glassware, a mixture of barium sulphate, sulphide and carbonate has been patented by E. E. Fisher (U. S. Patents 1,665,693 and 1,665,594). It is claimed that this mixture is particularly beneficial where sharp corners and intricate patterns have to be completely filled. It should be noted that the barium chemicals used in glass-making must be virtually free of iron, silica and dolomite.

GENERAL USE OF BARITE AND BARIUM COMPOUNDS IN LAKE PIGMENTS AND DYEING

Barite is used as a base for lakes; while barium chloride and blanc fixe are extensively used as reagents for the precipitation of lakes. The name lake is used to denote the large and important class of pigments obtained by precipitating an organic dyestuff as an insoluble compound on a mineral base. The word lake is derived from "lacca", the term given by the medieval dyers to the insoluble scum which formed in dye vats by the interaction of the excess of dye with the metallic salts used for mordanting. This was found to yield a useful pigment, and was collected and sold to artists. It was used as a pigment until the introduction of synthetic dyes, which have gradually replaced them.

At present, the greater part of lake pigments is prepared from these artificial dyes, and most of the natural lakes are obsolete and only of historical interest. A few, however, require brief reference as being still in use to a limited extent, notably the pigments derived from cochineal, logwood, madder, and indigo.

The introduction of synthetic dyes prepared from coal tar, at once widened the field of lake pigments also, with the result that a constantly increasing number of such lakes were produced. These succeeded the old lakes prepared from natural dyes.

Lakes from Synthetic Dyes

Lake pigments are produced from synthetic dyes in a wide range of color, covering the complete spectrum from red to blue; and including black and brown tints. The conversion of the soluble dye into a pigment is a process of simple precipitation. By reaction with a soluble metallic salt, the soluble dye is precipitated as the insoluble compound of the metal with the dye radical.

In the manufacture of lakes, therefore, three fundamental materials are involved: The dyestuff, the precipitating agents, and the mineral bases. Barite and its salts are used as both the precipitating agents and the mineral bases.

Dyestuffs: Of the great number of dyestuffs, only a few are suitable for preparing lakes. Those used for lake manufacture may be grouped as follows, according to the method of precipitation:

1. Acid dyes - those which can be precipitated from solution by soluble metallic salts, such as barium chloride, and aluminum sulphate.
2. Basic dyes - those which can be precipitated by acids, such as tannic, phosphoric and arsenous acids. Typical members of this group are methyl violets, magenta, methylene blues, and malachite green.
3. Insoluble or pigment dyes - those in which no precipitation is required. They are reduced by grinding with a mineral base.
4. Adjective dyes - those which though not colored give colored lakes. This class includes the fast lakes from alizarine and its derivatives.

Precipitating Agents: The reagents used with acid dyes are as follows:

1. Barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$). This is used for obtaining colorless rhombic crystals which should be neutral and free of iron. It is soluble in water and the solution is poison.

2. Lead acetate ($\text{PbAc} \cdot 3\text{H}_2\text{O}$), molecular weight 379. It is soluble in water, forming a highly poisonous solution. It is known as sugar of lead on account of its sweet taste.

3. Lead nitrate ($\text{Pb}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$).

4. Aluminum sulphate ($\text{Al}_2(\text{SO}_4)_3$).

The precipitating agents for basic dyes are:

1. Tannic acid.

2. White arsenic (As_2O_3).

3. Fatty acids.

4. Di-sodium hydrogen phosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$).

Mineral Bases:

(a) Method of Introducing a Base into a Lake:

1. By simultaneous precipitation with the dye, where barium chloride is used as a precipitating agent. For instance, soluble sulphates may be introduced into the dye solution so as to precipitate barium sulphate at the same time as the lake.

2. By suspending them in the solution from which the dye is to be precipitated.

3. By dry-grinding with the dye.

(b) Base Material:

1. Barite. Only the best grades of barite are admissible. Purity of color, freedom from iron and oversize particles are essential. Barite is used as a base largely on account of its cheapness and lack of opacity. It produces cheap lakes of bright full color with a minimum of dye.

2. Blanc Fixe is generally used for lake-making in pulp form, containing about 20 per cent of water. The pulp is reduced with water to a thin cream and added to the dye solution before precipitation.

The blanc fixe should be tested for free acidity, which is a common impurity owing to its method of preparation. It produces much softer lakes than barite because of the smaller size of its particles. However, with equal amounts of the same dye, barite produces a brighter and fuller color than blanc fixe. With both, the lakes are practically transparent in oil although they possess good body when used with water mediums. For the production of lakes to be used as oil colors they are largely used in conjunction with lead sulphate, and for printing uses with alumina.

3. There are many other materials that can be used as bases for lakes, such as China clay, calcium sulphate, alumina, satin white, and zinc oxide.

BARIUM IN ELECTRIC STEEL PRACTICE

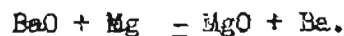
M. A. Baerstein*, of the National Pigments and Chemical Company of St. Louis, has claimed that an addition of a mixture of barium carbonate and barium oxide, about half an hour before pouring, greatly improves the product of heats of ferrous metals and adds considerably to the life of the acid lining of an electric furnace. It is also claimed that the presence of these compounds of barium produce a more quiet and steadier arc. When high percentages of sulphur are present the barium compounds are said to reduce the amount of sulphur appreciably. Less viscous slags are also produced, resulting in less slag inclusions in the products.

*Iron Age, vol. 134, no. 23, Dec. 1934, p. 32.

BARIUM METAL

Unlike the majority of metals, barium, though very useful in some of its compounds, has few practical applications as a metal. As a pure element it has a metallic appearance with a yellowish reflex, a specific gravity of 3.75 and melts at 1150° C. It decomposes water more energetically than calcium and strontium.

Barium can be obtained in the metallic state by the electrolysis of molten barium chloride in the presence of ammonium chloride. A newer and better electrolytic method, however, is the electrolysis of a barium chloride solution in which mercury is used as a cathode and forms an amalgam. The amalgam is then distilled in a current of hydrogen, the barium hydride thus formed losing its hydrogen when heated in vacuo, so that pure barium remains (Guntz, 1907). It is also obtained by heating barium oxide with magnesium:



According to Guntz, this can be done better with powdered aluminum, thus: $3\text{BaO} + 2\text{Al} = \text{Al}_2\text{O}_3 + 3\text{Ba}$

It can be done most economically (C. Matignon, 1913) by placing compressed pastille of a mixture of barium oxide and powdered silicon (or ferrosilicon) in a steel tube, evacuating the latter and heating it inside a porcelain tube in an electric furnace at 1200° C: $3\text{BaO} + \text{Si} = \text{BaSiO}_3 + 2\text{Ba} - 18,500 \text{ cal.}$; the barium vapor condensing in the cold part of the steel tube outside the furnace. The product thus obtained is 98.5 per cent pure.

Uses

Metallic barium is used in the manufacture of radio tubes and in the preparation of certain alloys. One of the most important of these alloys is "Frary metal", which contains lead, barium, and calcium. This alloy is used as a bearing metal.

Price

The market price of barium metal is high and unstable, being entirely out of line with the low price of its various compounds. Twenty years ago barium cost from \$500 to \$2350 per pound, depending on the purity of the product. Today the price is around \$5.00 per pound.

ALLOYS OF BARIUM

One of the main reasons why the early incandescent lamps were so expensive was because it is uneconomic to attempt to obtain a very good vacuum by an ordinary vacuum pump. In order to improve the vacuum obtainable with the pumps, small quantities of chemicals are introduced into the glass lamp bulbs that have the attribute of readily combining with residual gasses. These chemical substances are known as "getters." They not only make for superior vacuums but cheapen the making of incandescent lamps and radio tubes immeasurably.

Several elements are in wide use today in this field, including phosphorus.* An alloy of barium and aluminum is also being used quite a lot now. In this case the active material is vaporized from the alloy and takes part in a combination with the gases at an elevated temperature. The active material being the barium. Copper-clad barium is also used for this same purpose; the copper covering being for the purpose of preventing too violent a reaction. The "getter", in the form of the barium alloy, is fastened at a convenient place inside of the bulb or tube and its dispersal carried out by heating this spot with a pointed flame.

"Batalum" Getter**

During the course of research work on thermionic emitters, a method of producing very pure alkali earth metals was discovered. The method has led to the development of Batalum getter which has been found to satisfy the requirements for a getter for vacuum tubes.

*Malagnani, U. S. Patent 537,693, Apr. 16, 1895.

**"Batalum", a Barium Getter for Metal Tubes, by E. A. Lederer and D. H. Wamsley (Radio Corporation of America).

The Batalum getter consists essentially of a length of tantalum wire coated with a mixture of barium carbonate and strontium carbonate. The name Batalum was derived from a combination of syllables from barium and tantalum. Barium and strontium metals are obtained by heating the tantalum wire electrically. The carbonates of barium and strontium are changed to the respective oxides at 800 to 1000° C. The tantalum wire reduces the oxides to produce barium and strontium metal at a temperature about 1200° C. Approximately 40 per cent of the theoretical yield is obtained. This relatively low yield is probably explainable by the formation of stable tantalates of barium and strontium.

Since barium metal is very active chemically, and, unlike magnesium, unprotected by its own oxide, a new technique for its introduction into the tubes had to be developed. The following methods have been, or are being, used to this end commercially:

1. Thermal decomposition of bariumazide.
2. Copper, nickel or aluminum-clad barium metal. (A metal tube filled with barium metal and the ends of the tube pinched nearly air-tight).
3. Barium-magnesium and barium-aluminum alloy, both of which are essentially unaffected by the atmosphere at room temperature.
4. Production of barium by means of chemical reaction carried out in vacuum. (For example, reduction of barium oxide by aluminum or silicon).

The above methods were developed for use in making radio receiving tubes with glass envelopes. "Flashing" (or dispersal) of the getter was carried out by high-frequency heating of a suitable getter holder.

Though the use just referred to has become quite important, its consumption of barium is comparatively small, that is on a tonnage basis. Further developments along these lines cannot, therefore, be expected to greatly influence the demand and consumption of crude barite and witherite.

Prices

Prices on barium alloys must be obtained specially from the makers, as they fluctuate in wide ranges and new alloys sometimes appear over night to displace those in popular use.

TOXIC EFFECTS OF BARIUM SALTS

In discussing any group of chemical compounds it is important to note where they are disadvantageous as well as useful. The soluble barium salts are toxic*, but very widely in degree in this respect. Barium carbonate, nitrate, chloride and sulphate are very poisonous; but the hydroxide is only slightly so. Recorded cases of poisoning give the following facts: (1) "6.5 grams of barium chloride have destroyed the life of an adult woman in 15 hours; (2) 14 grams of barium nitrate have killed a man in 6.5 hours; (3) and the carbonate of barium has destroyed a person in the relatively small dose of 3.8 grams."

The local physiological action of barium salts are as follows:

1. Malaise, nausea, salivation, vomiting and pain in the stomach.
2. Excitation of the alimentary canal, both of the nervous and muscular apparatus; hence vomiting, painful colic, and acute diarrhoea.
3. Excitation of the brain motor centers.
4. Weakness or destruction of the power of muscular contraction.

No record of a poisonous case concerning barium hydroxide can be found. Before 1903 it was used to extract the sugar from molasses in Europe, but no recorded poisonings took place.

*Blyth, M. W., "Poisons; Their Effect and Detection"; Charles Griffin and Co., Exeter St., Strand, England, 1906, p. 711.

CUSTOMS TARIFF RATES ON IMPORTS OF CRUDE BARITE
AND BARIUM PRODUCTS INTO THE UNITED STATES.

(Effective January 1st., 1936).

Crude Barite.....\$4.00 per ton (long ton; 2 tons minimum lot).

Ground Barite \$7.50 " " "

Crude Witherite: (a) unground.....free.

(b) ground.....30% ad valorem.

Lithopone: (a) containing less than 30% ZnS.....1 $\frac{3}{4}$ cts.lb.

(b) " over 30% "...1 $\frac{3}{4}$ cts.lb. + 15%.

All Barium Alloys.....25% ad valorem.

Blanc fixe.....1 $\frac{3}{4}$ cts.lb.

Barium carbonate, pptd......1 $\frac{1}{2}$ cts.lb.

" chloride.....2 "

" dioxide.....6 "

" hydroxide.....1 $\frac{1}{4}$ "

" nitrate.....2 "

" oxide.....2 $\frac{1}{2}$ "

All barium compounds not elsewhere specified: 25% ad valorem.

IMPORTS AND EXPORTS OF BARIUM COMPOUNDS.

Generally speaking, the United States is an importer of barium compounds, despite its important position as a world producer. This is nothing unusual, however, when one considers the vast domestic market and industrial machine of this country. The imports, too, though overbalancing exports, are only a small percentage of the total barite and barium compounds produced and marketed domestically. The accompanying table and graph gives actual figures on this phase of the subject.

UNITED STATES IMPORTS and EXPORTS of BARIUM COMPOUNDS, 1929-1939, in Short Tons (a).

<u>Ba Compound</u>	1929	1930	1931	1932	1933	1934	1935	1936	1937	1938	1939
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Lithopone:

(a) Imports.	8409	7018	5674	4724	5596	3927	4603	4781	5801	3932	2641
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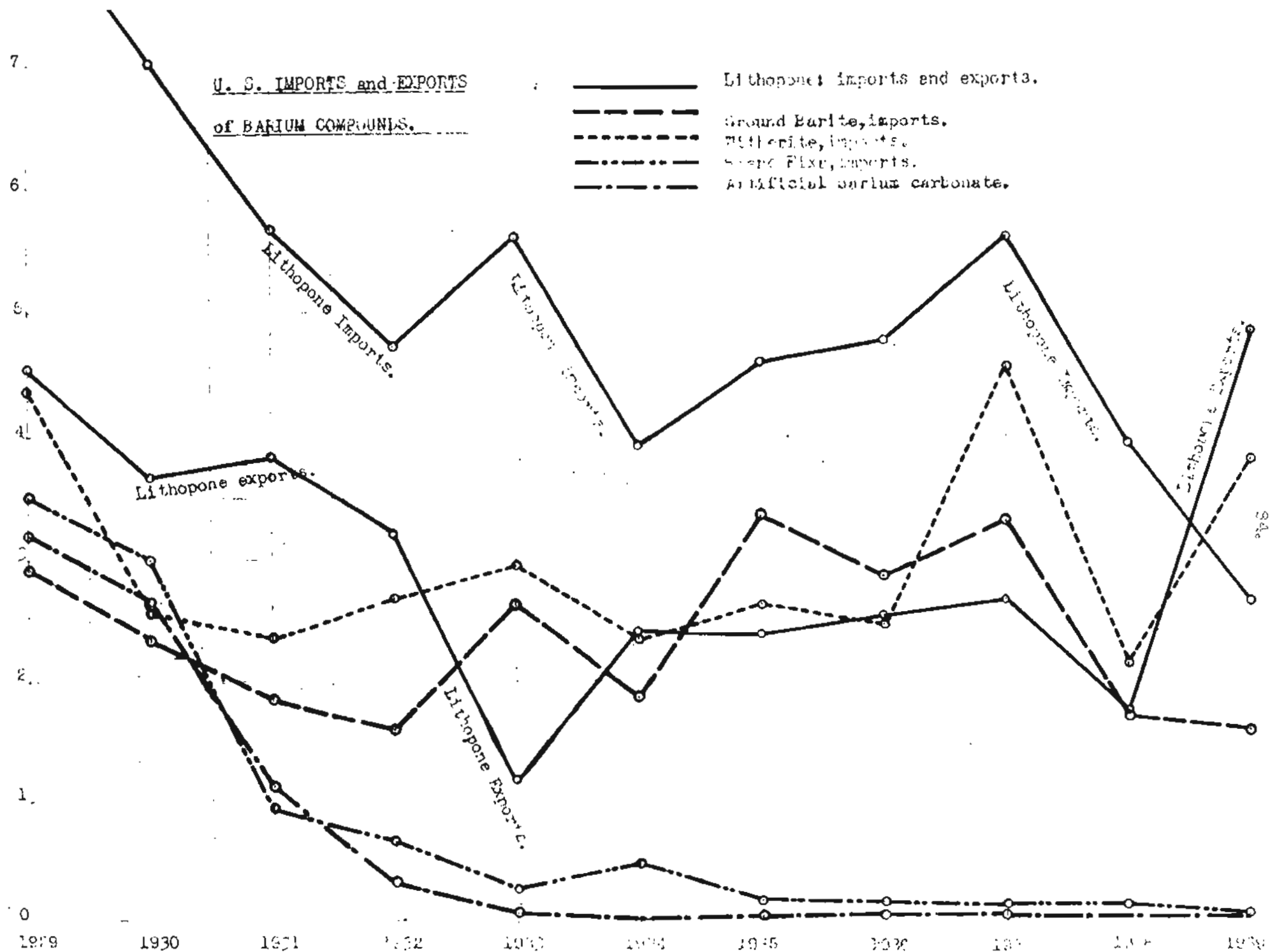
(b) Exports.	4556	3665	3821	3212	1186	2401	2372	2538	2871	1734	4845.
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Imports:

Ground barite	2924	2331	1851	1594	2632	1863	3354	2873	3313	1700	1590.	(a) Data taken from <u>Minerals Yearbook</u> : 1932-33 p.761; 1935, pp 1133 and 1134; 1939,p.1328.
Blanc fixe	3501	2994	930	656	245	459	141	123	109	106	38.	
Art. carbonate	3806	2662	1110	303	49	11	30	30	
Witherite	4376	2562	2352	2880	2949	2358	2834	2464	4556	2115	3819.	
Chloride	78	7	6	39	6	107	392	244	315	69	39.	
Nitrate	615	407	423	330	359	454	258	185	157	128	
Hydroxide	202	220	345	235	281	287	271	370	310	236	380.	
Dioxide	0.06	0.01	0.06	0.16	1.0	0.18	0.22	0.69	0.11	0.05	0.17.	
Oxide	221	0.01	110	0.06	0.015	0.14	0.15	0.01	
Others n.e.s.	8	4	8	8	28	50	27.	

U. S. IMPORTS and EXPORTS
of BARIUM COMPOUNDS.

————— Lithopone imports and exports.
 - - - - - Ground Barite, imports.
 - - - - - Witherite, imports.
 - Selenic Fluor, imports.
 - Artificial barium carbonate.



PRICE RANGES OF SOME STANDARD GRADES OF BARIUM COMPOUNDS, in cents per pound. (a).

Barium Compound.	1930	1931	1932	1933	1934	1935	1936	1937	1938	1939	1940
Barite, floated, domestic bbls. c.l. St. Louis.	1.15	1.15	1.15	1.15	1.15	1.15	1.19	1.19	1.18	1.18	1.21.
" German, grd. bbls. c.l. ex-dock				1.15-20	1.2	1.2	1.2-.25	1.25.	1.25	1.25	No price.
" Italian, ground, bbls c.l. ex-dock					1.5	1.5	1.5	1.5	1.5	1.5	"
Witherite, natural, 90-96% BaCO ₃ , ground.	2.2	2.2	1.9-2.2	1.9-2.15	2.25	2.1	2.1	2.1-2.2	2.05-.15	2.05-.15	2.25-.35
BaCO ₃ , precip. bgs. c.l works	2.9-3.0	2.9-3.0	2.8-2.9	2.8-3.05	2.8-3.05	2.8-3.05	2.8-3.05	2.6-3.1	2.62	2.62	2.62-.75
" , sulphur free, bgs. bbls. c.l. works								2.6-3.1	2.87-3.12	2.87	2.77
Barium Hydroxide, bbls. (Hydrate)	4.75-5.5	4.75-5.5	4.25-5.5	4.25-5.25	4.75-6	5-6	5-7.5	4.75-5.5	4.75-5.5	4.75-5.75	5.5-7
BaCl ₂ , tech. domestic, cryst. bags, c.l.	3.1-3.2	3.1-3.2	3.1-3.2	3.6-3.7	3.6-4.35	3.6-4.35	3.6-4.65	3.6-4.85	3.85-5.1	3.85-5.1	3.85-5.1
" C.P., cryst. bbls.	17-18	17-18	17-18	13-16	13-14	13-20	18-20	18-20	18-20	19-25	25.
BaClO ₄ , kegs.	14-15	14-15	13.75-15	13.75-16	15-16	14-17.5	15.5-17.5	15.5-17.5	16.5-17.5	16.5-17.5	20-25.
BaO, ground, drums	12	12	10-12	10-12	10-12	10-13	11-15	11-15	9-11	9-11	9-15
BaO ₂ , drums.	12-13	12-13	11-13	11-13	11-13.	11-15	11-15	11-15	11-15	11-15.	10-15
BaF ₂	12-20	12-13	12-13	12-16	15-16	15-16	15-16	15-16	11.5-12.5	11.5-12.5	14-15
BaSiF ₆ , barrels.			15	15-16	15-16	15-16	15-16	15-16.	11.5-12.5	11.5-12.5	16.
Ba(NO ₃) ₂ , cascs.	7.50-8.25	7.25-8	7-8	7.25-8.5	8.25	8.25	7-8.25	7-8.25	6.75-7.25	6.75-7.25	8.5-105
Ba(SO ₄) ₂ , tech. (Hl. fixe) X-Ray, in barrels.	10-15	10-11	10-11	10-11	13	13	13	9.5-13	9.5-10	9.5-10.5	9.5-10.
Lithopone, ordinary, domestic, delvd. bags.	5.25 -5.5	4.5-4.75	4.5-4.75	4.5-5	4.5-4.75	4.5-4.75	4.5-4.75	4.25-4.62	4.12-4.62	4.12	3.6-3.85.
Lithopone, domestic, high-strength, bags.					6-6.25.	6-6.25	6-6.25	5.75-6.12	5.62- 6.12.	5.62- 5.97.	5-5.25.
Lithopone, titanated, bags.					6-6.25	6-6.25.	6-6.25	"	"	"	"

(a) OIL, PAINT, AND DRUG REPORTER, periodical - weekly issues 1930-40. All prices reduced to a pound basis for comparison.

ALPHABETICAL LIST OF PRODUCERS, MARKETERS and IMPORTERS of
BARITE and BARIUM COMPOUNDS in THE UNITED STATES.

- (1) Advance Solvents & Chemical Corp., S.E. Cor. 28th. & 5th. Ave., N.Y.C.
- (2) Aluminium Co. of America, 1856 Gulf Bldg., Pittsburgh, Pa.
- (3) American Cyanamid & Chemical Corp., 30 Rockefeller Plaza, N.Y.C.
- (4) American Fluoride Corp., 151 W. 19th. St., N.Y.C.
- (5) American Oil & Supply Co., 239 Wilson Ave., Newark, N.J.
- (6) American, Zinc, Lead & Smelting Co., Paul Brown Bldg., St. Louis, Mo.
- (7) American Zinc Sales Co., Columbus, Ohio.
- (8) Baker, H.J. & Bro., 271 Madison Ave., N.Y.C.
- (9) Baker, J.T., Chemical Co., North Phillipsburg, N.J.
- (10) Balfour, Guthrie & Co., Ltd., 351 California, San Francisco, Cal.
- (11) Barium and Chemicals, Inc., Willoughby, Ohio.
- (12) Barium Products, Ltd., 405 Lexington Ave., N.Y.C.
- (13) Barium Reduction Corp., South Charleston, W. Va.
- (14) Belmont Smelting & Refining Works, Inc., 320 Belmont Ave., Brooklyn, N.Y.
- (15) Bond, Vivian & Co., 68 Beaver, N.Y.C.
- (16) Bugbird, H.C., Co., 120 Liberty St., N.Y.C.
- (17) Ceramic Color & Chemical Mfg. Co., New Brighton, Pa.
- (18) Chemical & Pigment Co., Inc., 6401 St. Helena Ave., Baltimore, Md.
- (19) Chemical Products Corp., Cartersville, Ga.
- (20) Chicago Copper & Chemical Co., Blue Island, Ill.
- (21) Chrystal, Chas. B., Co., Inc., 13 Park Place, N.Y.C.
- (22) Clinchfield Sand & Feldspar Corp., Hearst Tower Bldg., Baltimore, Md.
- (23) Commercial Minerals Co., 310 Irwin, San Francisco.
- (24) De Lore, Div. of National Pigments & Chemical Co., Iron Mt. tracks, St. Louis.

- (25) Dill, Marshall, 510 Montgomery (Mfrs.), San Francisco.
- (26) duPont, E. I., de Nemours & Co., Inc., (R. & H. Chemicals Dept.), 11th. and Orange Sts., Wilmington, Del.
- (27) Eagle-Picher Lead Co., 1935 Temple Bar Bldg., Cincinnati, Ohio.
- (28) Eastern Color & Chemical Co., 145 Nassau St., N.Y.C.
- (29) Foote Mineral Co., Inc., 1610 Summer St., Philadelphia, Pa.
- (30) Franks Chemical Co., Inc., Bush Terminal, Brooklyn, N.Y.
- (31) Grasselli Chemical Co., Guardian-Euclid Bldg., Cleveland, Ohio
- (32) Hamill & Gillespie, Inc., 225 Broadway, N.Y.C.
- (33) Harshaw Chemical Co., 1933 E. 97th. St., Cleveland, Ohio.
- (34) Hummel Chemical Co., Inc., 140 Cedar, N.Y.C.
- (35) Hurst, Adolphe & Co., Inc., 422 Lexington Ave., N.Y.C.
- (36) Import Chemicals Co., 164 1st. St., Jersey City, N.J.
- (37) Industrial Minerals & Chemical Co., Berkeley, Cal.
- (38) Innis, Speiden & Co., 121 Liberty St., N.Y.C.
- (39) International Salling Corp., Dept. T, 26-28 Beaver St., N.Y.C.
- (40) Jungmann & Co., Inc., 157 Chambers St., N.Y.C.
- (41) King, E. F. & Co., Inc., 405 Atlantic Ave., Boston, Mass.
- (42) Krebs Pigment & Color Corp., Thomas & Vanderpool Sts., Newark, N.J.
- (43) Lavino, E. J., & Co., 1528 Walnut St., Philadelphia, Pa.
- (44) Lookout Point Mfg. Co., Chattanooga, Tenn.
- (45) Los Angeles Chemical Co., 1960 Santa Fe Ave., Los Angeles, Cal.
- (46) Mallinkrodt Chemical Works, 2nd. & Mallinckrodt Sts., St. Louis, Mo.
- (47) McGean Chemical Co., Republic Bldg., Cleveland, Ohio.
- (48) McNulty, Jos. A., 116 Liberty St., N.Y.C.
- (49) Mephram, Geo. S. Corp., E. St. Louis, Ill.
- (50) Merck & Co., Inc., 1935 Kerrigan Rd., Rahway, N.J.

- (51) Minerals & Insulation Corp., 108 Mercer St., N.Y.C.
- (52) Monmouth Chemical Corp., 140 Cedar St., N.Y.C.
- (53) Muller, Wm. H. & Co., Inc., 122, E. 42nd. St., N.Y.C.
- (54) New Jersey Zinc Sales Co., Inc., Front & Fletcher Sts., N.Y.C.
- (55) New Riverside Ochre Co., Cartersville, Ga.
- (56) Ore & Chemical Corp., 80 Broad (Imp.), N.Y.C.
- (57) Osborn, C. J. & Co., 132 Nassau, N.Y.C.
- (58) Philipp Bros., Inc., 70 Pone St., N.Y.C.
- (59) Reichard-Coulston, Inc., 95 Madison Ave., N.Y.C.
- (60) Rowley, Geo. A. & Co., 937 N. Front St., Philadelphia, Pa.
- (61) Salomon, L. A. & Bro., 216 Pearl (Imptrs. & Dealers), N.Y.C.
- (62) Schundler, F. E. & Co., Inc., 606 Railroad St., St. Louis, Mo.
- (63) Smith Chemicals & Color Co., Inc., 55 John, Brooklyn, N.Y.
- (64) Smith, Frank, Cartersville, Ga.
- (65) Smith, J. Lee & Co., Inc., 23 Jacob, N.Y.C.
- (66) Southern Mining Co., Cartersville, Ga.
- (67) Superior Mineral Co., Cadet, Mo.
- (68) Synthetic Iron Color Co., Richmond, Cal.
- (69) Thompson, Weinmann & Co., Cartersville, Ga.
- (70) Turner, Joseph, & Co., 500 5th. Ave., N.Y.C.
- (71) Uhlich, Paul, & Co., 157 Chambers St., N.Y.C.
- (72) United Color & Pigment Co., Evergreen Ave., Newark, N.J.
- (73) Vitro Mfg. Co., 60 Cliffe St., Corliss Sta., Pittsburgh, Pa.
- (74) Wagner, Charles A. & Co., Inc., 811 Callowhill St., Philadelphia, Pa.
- (75) Warner Chemical Co., 403 Lexington Ave., N.Y.C.
- (76) Western Talc Co., 1901 Slanson Ave., Los Angeles, Cal.

- (77) Westvaco Chlorine Products, Inc., Chrysler Bldg., N.Y.C.
 - (78) Whittaker, Clark & Daniels, Inc., 260 West Broadway, N.Y.C.
 - (79) Williams, C.K. & Co., 13th. St. & Bushkill Creek, Easton, Pa.
 - (80) Wisniewski-Tumpear, Inc., 295 Madison Ave., N.Y.C.
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